BRIEF NOTES

OF

CHEMICAL FACTS.

LONDON : PRINTED BY
SPOTTISWOODE AND CO., NEW-STREET SQUARE
AND PARLIAMENT STREET

OUTLINES OF CHEMISTRY

OR

BRIEF NOTES OF CHEMICAL FACTS.

BY

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LONDON:
LONGMANS, GREEN, AND CO.
1870.

PREFACE.

THIS BOOK consists substantially of the notes from which I have lectured for the last seven years at St. Bartholomew's Hospital; revised, and somewhat extended, so as to place before the student a connected outline of the leading Facts of Chemistry, in their relations to each other. It is essentially descriptive in character; and aims at calling to mind, in as few words as possible, the ascertained origins, properties, and metamorphoses of the chemical substances to which it refers. The earlier sheets have been struck off at different periods within the last two years, as I could afford time for their preparation and revision. To the later sheets I have devoted myself uninterruptedly during the past autumn vacation.

The main object, with which I undertook the work, was to furnish the students of St. Bartholomew's with an abstract of my own lectures. It is accordingly not intended for study by itself; but as a companion to the teachings of the lecture room, and as an aid to the appreciation of

more complete works, such as Miller's Elements and Watts's Dictionary, to both of which I am largely indebted.

In the present unsettled state of chemical notation and nomenclature, I think it right to add a few words explanatory of the course which I have adopted in relation thereto.

Throughout the book, but especially in the later chapters, I have made considerable use of the modes of expression advocated more particularly by Dr. Williamson. But while freely employing such terms as ferrous sulphate, cupric nitrate, zinc chloride, &c., I have not thought it necessary, nor do I think it advisable, to discard altogether the older modes of expression, sulphate of iron, nitrate of copper, chloride of zinc, &c. In so unimportant a matter as this, I have no desire to limit myself to one particular set of phrases; and, accordingly, I use in the book, as I have both the habit and the intention of using in oral address, the two sets of terms indifferently and alternatively.

Again, without in any degree wishing to proscribe the use of names expressing the quantified composition of individual bodies,—indeed such names cannot be altogether dispensed with,—I much prefer for general use those other names which, by a well-understood convention, express mainly the relations of bodies to one another; and here also I have the advantage of being at accord with Dr. Williamson. For example, although I have no doubt

whatever that corrosive sublimate is really a di-chloride of mercury, there was a time when I was equally certain of its being a mono-chloride; and, taught by this experience, I now prefer to distinguish it by the name 'mercuric chloride,' and calomel by the name 'mercurous chloride,' whereby I merely imply, what never has been a matter of question, that the ratio of chlorine to mercury is greater in the one compound than in the other. Similarly I prefer to distinguish the several chromium oxides by the prefixes chromous, chromic, and chromate, rather than by the suffixes mon-oxide, sesqui-oxide, and ter-oxide. It is an obvious consequence of this method of nomenclature that dissimilarly constituted bodies should frequently be expressed by similarly constructed names; and, conversely, that similarly constituted bodies should be expressed by dissimilarly constructed names. Thus the dissimilarly constituted oxides CuO, Fe_2O_3, and SnO_2, are spoken of as cupric, ferric, and stannic oxides respectively.

The preference habitually accorded by different chemists to trivial or to systematic names for general use, is largely a matter of individual liking. For myself, I like, where they are sufficient for the purpose, to employ such trivial names as nitre, alum, potash, borax, green-vitriol, bleaching-powder, sal-ammoniac, muriatic acid, prussic acid, alcohol, wood-spirit, marsh-gas, chloroform, acetic ether, phosgene, &c. &c., alternatively with the systematic names for the respective compounds. With regard to the sys-

tematic nomenclature of that very important class of bodies, the salts of hydrogen, such expressions as chloride of hydrogen, hydric nitrate, hydrogen oxalate, &c., as used by different chemists, are, I conceive, quite unobjectionable; but for myself, I prefer, save in special cases, to call the several bodies so designated by their familiar names hydrochloric acid, nitric acid, and oxalic acid respectively. Accordingly in this book, as in the writings of nearly all the living chemists of Europe and America, the word 'acid,' standing without qualification, always signifies a salt of hydrogen.

Throughout I have deliberately avoided the use of any method of graphic notation, such as that of Prof. Kekulé, and the more plastic system subsequently introduced by Dr. Crum-Brown. Used as the method is by these distinguished chemists, with caution, as a means of expressing and discussing the constitution of particular bodies, deducible from their formative and transformative reactions, I do not deny its occasional usefulness; notwithstanding the liability of it, especially in its otherwise preferential form, to create false images in the mind. But used as Dr. Crum-Brown's system is by others, to express with equal confidence the ascertained and unascertained constitution of all bodies whatsoever, it has I believe exerted, and still continues to exert a most prejudicial influence on the study of chemical science, by making the fanciful sticking together of variously

pronged disks of more importance than the investigation of phenomena.

Lastly, in this book, I have not attempted to be systematic, at the sacrifice of simplicity, by expressing all reactions 'molecularly'; and for the sufficient reason that, in the majority of reactions, I do not myself know what the molecular formulæ of the reagents and products concerned are, and do not think it worth while to make a pretence of knowing.

In a book like this, abounding in formulæ, some errors of the press are almost unavoidable. I believe, however, that they will be found considerably under the average, thanks to the very careful revision which the proof sheets have been subjected to by my friend and former laboratory assistant Mr. W. H. Deering. The earlier sheets have had the additional advantage of being read over and criticised by my experienced friend Mr. Henry Watts, F.R.S., to whose invaluable Dictionary of Chemistry I have previously expressed my obligations.

WILLIAM ODLING.

ROYAL INSTITUTION:
October 18th, 1869.

Errata.

Page		*Line*		*Error*		*Correction*
23	..	4 from bottom	..	Cl_2Hg_2O	..	$Cl_2Hg_4O_4$
27	..	5 from top	..	NaF_4Al	..	Na_3F_6Al
144	..	17 ,,	..	0·4	..	[illegible]·4
255	..	9 ,,	..	calc-spar	..	talc-spar

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CHEMISTRY.

CHAPTER I.

(1.) Elastic Fluids.

Material objects viewed in relation to their composition. Recognition of the different kinds of matter of which all bodies are constituted. Comparison of physical with chemical changes. Special reference of chemistry to changes in the composition or identity of bodies. Consequent developments of motion, heat, and electricity.

Different physical states of aggregation. Existence of same matter in solid, liquid, and gaseous forms, illustrated by ice, water, and steam. More or less persistent states of certain bodies, as charcoal, lime, alcohol, marsh-gas, air, &c.

Independently of specific differences of kind, materiality of gaseous bodies shown by their impenetrability, inertia and weight. Weight of 1 litre of air, under normal conditions, 1·3 grammes nearly: or weight of 100 cubic inches of air, 31 grains.

System of metrical weights and measures. Metre equal to 39·37 inches; divisible into 10 decimetres, 100 centimetres, and 1000 millimetres. Millimetre equal to ·039, or $\frac{1}{25}$ of inch nearly.

Litre, or cubic decimetre, equal to 1·76 pints; divisible into 1000 cubic centimetres. Cubic centimetre equal to ·061, or $\frac{1}{16}$ of cubic inch nearly.

Kilogramme, equal to 2·2 pounds; divisible into 1000 grammes. Gramme, or weight of cubic centimetre of water at 4° C., equal to 15·4 grains.

Atmospheric pressure, a result of the weight of air. Accumulated weight of each successive stratum pressing in every direction. Weight of any column of atmosphere equal to that of similar column of water about 10 metres high, and to that of similar column of mercury 760 millimetres, or 30 inches high. Principle of the barometer.

Weight of a column of mercury of 1 square centimetre area, and 760 millimetres height, equal to rather more than 1 kilogramme. Hence ordinary atmospheric pressure equal to 1·033 kilogramme on square centimetre, or 15 lbs. on square inch.

Elasticity of air and gases in general. Extension or compression of definite quantity or weight of air into any given space. Principle of the air-pump and condensing syringe. Bulk inversely, density and elastic force of air directly, as pressure upon it. Decrease in density of atmosphere with height. Constant balance of pressure and elasticity.

Observation of pressure in measurement of gases standing over mercury or water. Difference in millimetres between internal and external level of mercury subtracted from or added to 760 millimetres, or height of barometer at time. Pressure of 1 millimetre of mercury equal to that of 13·6 millimetres of water. Correction according to ordinary rule of inverse proportion, as of 100 c.c. at 722 mm., for instance:

$$760\text{mm.} : 722\text{mm.} :: 100\text{c.c.} \quad 95{\cdot}0\text{c.c.}$$

Expansion, or correlative increase in elasticity, of air and gases by heat. Increment of expansion in gases, ·003665 or $\frac{1}{273}$ of bulk at 0°, for every centigrade degree. Hence 273 c.c. at 0° become 273+1 c.c. at 1°, 273+10 c.c. at 10°, 273+100 c.c. at 100°, and 273+273 c.c. at 273°. Consequent correction of gaseous bulk for temperature, as of 95 c.c. at 20° to *x* c.c. at 15°, according to proportion:

$$273 + 20 : 273 + 15 :: 95{\cdot}0 : 93{\cdot}4$$

In gas at constant volume, increase of $\frac{1}{273}$ of elasticity at 0° for every centigrade degree. Hence, under constant volume, elasticity doubled, under constant pressure, volume doubled by increase of temperature from 0° to 273°.

(2.) Symbolic Notation.

Classification of chemical substances into elements and compounds. Bodies, not resoluble into two or more different kinds of matter, distinguished as simple or elementary. General characters of the sixty elements, metallic $\frac{4}{5}$, non-metallic $\frac{1}{5}$. Their different states of aggregation. Hydrogen, chlorine, oxygen, and nitrogen gaseous; bromine and mercury liquid; the remainder solid.

Nature of definite chemical compounds. Their characteristic homogeneity, and fixity of composition. Highly stable compounds produced by union of oppositely characterised elements. Stylous, or electro-negative, or chlorous, contrasted with basylous, or electro-positive, or alkalous elements. The difference one of seriation, or degree.

Assignment to every element of a particular number, indicating its smallest combining proportion, or atomic weight. The proportional number of hydrogen taken as unity. Other proportional numbers, integer multiples of that of hydrogen or its moiety (?).

H	Hydrogen	1	Cl	Chlorine	35·5
Na	Sodium	23	O	Oxygen	16
Ag	Silver	108	N	Nitrogen	14
Cu	Copper	63·5	C	Carbon	12

Respective combining proportions of different elements represented by their symbols or abbreviated names. Representation of 1 part by weight of hydrogen by the symbol H; of 23 parts by weight of sodium by the symbol Na; of 35·5 parts by weight of chlorine by the symbol Cl, &c.

Combination of elements with one another only in the ratios of their proportional numbers, or of multiples of those numbers:

Hydrogen & chlorine	1	+	35·5
Hydrogen „ copper	1	+	63·5
Chlorine „ copper	{ 35·5	+	63·5
	(35·5)2	+	63·5

Consequent expressibility of definite compounds by allocations of elementary symbols, as HCl, HCu, ClCu, Cl_2Cu, &c. Meaning of so-called chemical formulæ.

Proportional number, or atomic weight, of a compound body, the sum of the atomic weights of its constituent elements. Atomic weight of common salt, NaCl, $23 + 35·5 = 58·5$; of lunar caustic, $AgNO_3$, $108 + 14 + 16 \times 3 = 170$. Chemical reactions, as of common salt with lunar caustic, represented by equations:

$$NaCl(58·5) \quad + \quad AgNO_3(170) \quad = \quad AgCl(143·5) \quad + \quad NaNO_3(85)$$

Reaction limited to atomic proportions of reagents. Any excess of either unaffected.

Multiple proportions of elementary atoms, or of constituent groupings, expressed by small figure to right of symbol, as NH_3 ammonia; NH_4Cl sal-ammoniac; $N(CH_3)_3$ tri-methylamine. Occasional breaking up of formulæ by periods, brackets, parentheses, &c., as $NH_3.HCl$; $\underbrace{NH_3}HCl$; $(NH_3)HCl$, &c. Multiple proportions of isolated compounds expressed by large figure to left of allocation of symbols, as $2NH_3$; $2(NH_3.HCl)$.

(3.) Law of Volumes.

Absorption of about one-fifth of the bulk of atmospheric air by ordinary combustibles, mercury when heated, and various bodies. Residual four-fifths of air, or n i t r o g e n, characterised by its inertness.

Recovery of absorbed one-fifth of air, or o x y g e n. Rapid burning of ordinary combustibles in oxygen. Reproduction of atmospheric air by mixture of oxygen and nitrogen gases.

Nature of ordinary combustion. Oxidised products obtained by burning various bodies in air or oxygen. Production of carbanhydride gas by combustion of carbon. Its detection in the air by means of lime-water.

Presence of water or moisture in the air shown by its condensation on cold surfaces. Water a compound of hydrogen and oxygen gases, and product of the combustion of hydrogen in oxygen or air. Indirect combination of hydrogen with nitrogen to form ammonia, and with carbon to form marsh-gas, &c.

Chlorine gas, a constituent of common salt. Combustion of hydrogen in or with chlorine to form hydrochloric acid.

Bulk of 1 gramme of hydrogen at 0° C. and 760 mm., 11·2 litres, or one gas-volume. Under same conditions weight of 11·2 litres of chlorine 35·5 grammes, of oxygen 16 grammes, and of nitrogen 14 grammes. Hence specific gravities, or equal volume weights, of hydrogen, chlorine, oxygen, and nitrogen 1, 35·5, 16, and 14 respectively. Consequent identity of numbers representing specific gravity and combining proportion of the elementary gases.

Combination of 35·5 parts by weight, or 1 volume, of chlorine with 1 part by weight, or 1 volume, of hydrogen to form hydrochloric acid.

Combination of 16 parts by weight, or 1 volume, of oxygen with 2 parts by weight, or 2 volumes, of hydrogen to form water.

Combination of 14 parts by weight, or 1 volume, of nitrogen, with 3 parts by weight, or 3 volumes, of hydrogen to form ammonia.

Combination by volume of carbon, as in marsh-gas and carbanhydride, hypothetical.

Specific gravity, or weight of one volume, of hydrochloric acid gas found to be $18·25, = \frac{36·5}{2}$. Hence weight of two volumes of hydrochloric acid gas identical with weight of one volume of

hydrogen 1, plus that of one volume of chlorine 35·5, = 36·5. Consequent non-alteration of volume by combination of hydrogen and chlorine gases with each other. Same result shown by direct experiment.

Specific gravity, or weight of one volume, of water-gas or steam found to be $9, = \frac{18}{2}$. Hence weight of two volumes of steam identical with weight of two volumes of hydrogen 2, plus that of one volume of oxygen 16, = 18. Consequent condensation of three volumes of mixed oxygen and hydrogen into two volumes of steam. Same result shown by direct experiment.

Specific gravity, or weight of one volume, of ammonia-gas found to be $8·5, = \frac{17}{2}$. Hence weight of two volumes of ammonia-gas identical with weight of three volumes of hydrogen 3, plus that of one volume of nitrogen 14, = 17. Consequent condensation of four volumes of mixed nitrogen and hydrogen into two volumes of ammonia. Same result shown by direct experiment.

The equality in bulk of all gaseous molecules an established law of physics. Unit of molecular bulk conventionally adopted by chemists, the bulk of two volumes, and unit of molecular weight, the weight of two volumes, or twice the specific gravity. Consequent representation of molecular weights and volumes of hydrochloric acid, water, and ammonia by the formulæ HCl, H_2O, H_3N; and of molecular weights and volumes of hydrogen, chlorine, oxygen and nitrogen by the formulæ H_2, Cl_2, O_2, and N_2.

Specific gravities or weights of one volume		Molecules or weights of two volumes	
H	1	H_2	2
Cl	35·5	Cl_2	71
O	16	O_2	32
N	14	N_2	28
$\frac{1}{2}HCl$	18·25	HCl	36·5
$\frac{1}{2}H_2O$	9	H_2O	18
$\frac{1}{2}H_3N$	8·5	H_3N	17
$\frac{1}{2}H_4C$	8	H_4C	16

(4.) Atomic Weights.

The smallest quantity of any particular element, whether or not of itself volatile, that is found to exist in two gaseous volumes of any of its compounds, taken as its atomic weight.

Atomic weights of hydrogen, fluorine, chlorine, bromine, iodine, oxygen, sulphur, selenium, tellurium, chromium, boron, nitrogen, phosphorus, arsenic, antimony, bismuth, carbon, silicon, titanium, tin, lead, mercury, cadmium, and osmium, determined in this manner,—all these elements forming one or more volatile compounds, of which the vapour-densities and centesimal compositions have been ascertained.

In case of non-volatile carbon, for instance, the specific gravity or single volume weight of marsh-gas found to be 8, and the molecular or double volume weight consequently 16. These 16 parts of marsh-gas shown by analysis to consist of 12 parts by weight of carbon, and 4 parts by weight, or 4 volumes, of hydrogen. Again, specific gravity or single volume weight of carbanhydride gas found to be 22, and its molecular or double volume weight consequently 44. These 44 parts of carbanhydride shown by analysis to consist of 12 parts by weight of carbon, and 32 parts by weight, or 2 volumes, of oxygen. Hence atomic weight of carbon 12, and formulæ of marsh-gas and carbanhydride, H_4C and CO_2 respectively.

Distinction between intensity of heat, or temperature, and quantity of heat. Measurement of quantity of heat by degrees of temperature imparted to, or lost by, given weight of water; or by weight of ice converted into water. Quantity of heat required to raise the temperature of 1 kilogramme of water 1 degree centigrade (from 0° to 1°), or to melt 12·5 grammes of ice, taken as the unit of heat.

In cooling from 100° to 0°, quantity of heat evolved by 1 kilo. of water 100 units; by 1 kilo. of iron, 11·4 units; by 1 kilo. of silver, 5·7 units; and by 1 kilo. of bismuth, 3·1 units; or, in round numbers, quantity of ice melted by 1 kilo. of iron

four times, and by 1 kilo. of silver twice that melted by 1 kilo. of bismuth.

Relative amounts of heat absorbed or evolved by different substances, when undergoing equal increments or decrements of temperature, known as their specific heats. Hence, for equal weights, specific heat of iron four times, and of silver twice that of bismuth.

Atomic weights, or smallest quantities existent in any two-volumes of vapour, of bromine, iodine, arsenic, antimony, bismuth, tin, lead, mercury, cadmium, zinc, &c. &c., found to be inversely as specific heats of equal quantities of the several elements; *i.e.* found to have approximatively the same specific heat, 6·2, as one another. Hence atomic weights of copper, silver, gold, and other metals not forming volatile compounds, determinable by their specific heats,—those weights of the different metals which have approximatively the same specific heat as 65 parts of zinc, 118 parts of tin, and 210 parts of bismuth, &c. &c., being selected as their respective atomic weights.

Atomic weights of lithium, sodium, potassium, silver, magnesium, aluminium, manganese, iron, cobalt, nickel, copper, thallium, gold, palladium, and platinum determined in this manner.

(5.) Equivalency.

Classification of primary hydrides into mono-, di-, tri-, and tetra-hydrides. Existence in two-volumes of each hydride of as many volumes of hydrogen as are indicated by its particular formula:

HF	H_2O	H_3N	H_4C
HCl	H_2S	H_3P	H_4Si
HBr	H_2Se	H_3As	
HI	H_2Te	H_3Sb	

Chlorine capable not only of uniting with, but also of replacing hydrogen, in proportion of volume to volume, with production of chlorides corresponding to above tabulated hydrides. Existence in two-volumes of each such non-metallic or semi-

Elements	Specific heats	Atomic weights	Specific heats of atomic weights	Formulæ of chlorides, &c.
Water	1·000			
Monads—				
Bromine	·084	80	6·74	HBr
Iodine	·054	127	6·87	HI
Lithium	·940	7	6·58	ClLi
Sodium	·293	23	6·75	ClNa
Potassium	·169	39	6·61	ClK
Silver	·057	108	6·15	ClAg
Diads—				
Sulphur	·177	32	5·68	H_2S
Selenium	·083	79·5	6·65	H_2Se
Tellurium	·047	128	6·11	H_2Te
Manganese	·122	55	6·69	Cl_2Mn
Iron	·114	56	6·37	Cl_2Fe
Cobalt	·107	59	6·31	Cl_2Co
Nickel	·108	59	6·41	Cl_2Ni
Copper	·095	63·5	6·04	Cl_2Cu
Magnesium	·250	24	5·99	Cl_2Mg
Zinc	·095	65	6·26	Cl_2Zn
Cadmium	·056	112	6·35	Cl_2Cd
Mercury	·032	200	6·38	Cl_2Hg
Triads—				
Phosphorus	·189	31	5·85	H_3P
Arsenic	·081	75	6·10	H_3As
Antimony	·051	122	6·19	H_3Sb
Bismuth	·031	210	6·47	Cl_3Bi
Aluminum	·214	27·5	5·87	Cl_3Al
Thallium	·033	204	6·81	Cl_3Tl
Gold	·032	196·5	6·37	Cl_3Au
Tetrads—				
Tin	·056	118	6·63	Cl_4Sn
Lead	·031	207	6·50	Et_4Pb
Palladium	·059	106·5	6·31	Cl_4Pd
Platinum	·032	197	6·39	Cl_4Pt
Osmium	·031	199	6·19	Cl_4Os

metallic chloride of as many volumes of chlorine as are indicated by its respective formula:

ClCl	Cl_2O	Cl_3N	Cl_4C
ClI	Cl_2S	Cl_3P	Cl_4Si

Metallic chlorides, owing to insufficient volatility, not often susceptible of vapour examination. Their similar classification on other grounds into mono-, di-, tri-, and tetra-chlorides, as instanced below. Existence of more complex chlorides, metallic and non-metallic; especially of sesquichlorides, as Cl_6C_2:

ClNa	Cl_2Zn	Cl_3Bi	Cl_4Sn
ClAg	Cl_2Hg	Cl_3Au	Cl_4Pt

Determination of exact quantity of any metal, &c., which can replace 1 part by weight of hydrogen in hydrochloric acid HCl, to unite with 35·5 parts by weight of chlorine, a question of analysis. Determination of atomic weight of metal, &c., as the single, double, treble, or quadruple of this quantity, and of formula of its chloride as a mono-, di-, tri-, or tetra-chloride, a question of vapour density where practicable, of specific heat, and of reactions.

Classification of elements, metallic and non-metallic, into monads, diads, triads, tetrads, &c. Their symbolic notation means of dashes, thus:—$\overset{\prime}{Ag}$, $\overset{\prime\prime}{Hg}$, $\overset{\prime\prime\prime}{Au}$, $\overset{\prime\prime\prime\prime}{Pt}$. Analogous graphic notation.

Exchange in one, two, three, and four atoms of hydrochloric acid, ClH, Cl_2H_2, Cl_3H_3, and Cl_4H_4 respectively, of one atom of hydrogen for one of silver, of two atoms of hydrogen for one of mercury, of three atoms of hydrogen for one of gold, and of four atoms of hydrogen for one of platinum to form compounds, $Cl\overset{\prime}{Ag}$, $Cl_2\overset{\prime\prime}{Hg}$, $Cl_3\overset{\prime\prime\prime}{Au}$, $Cl_4\overset{\prime\prime\prime\prime}{Pt}$ respectively. Consequent mono-, di-, tri-, and tetra- equivalency of atomic proportions of respective metals with regard to hydrogen. Occasional representation of their equivalent proportions by means of small letters, thus Ag′Cl, hg′Cl, au′Cl, pt′Cl, &c.

Atoms of even equivalency classed as artiads, of uneven equivalency as perissads. Combinations of different atoms

with one another by mutual saturation of respective equivalencies, as of $\acute{A}g_3$ with $\overset{'''}{Sb}$, of $\overset{'''}{Al}_2$ with $\overset{''}{O}_3$, of $\overset{''''}{C}$ with $\overset{''}{O}$ and $\acute{Cl}_2$ jointly, &c. Consequent even number of sum of equivalencies in compounds, as Ag_3Sb, Al_2O_3, Cl_2CO, &c.

Mono-, tri-, and penta-equivalency of same perissad element as nitrogen, in different compounds, as $\acute{N}_2O$, $H_3\overset{'''}{N}$, and $ClH_4\overset{v}{N}$? Di-, tetra-, and hexa-equivalency of same artiad element as sulphur, in $Cl_2\overset{''}{S}$, $Cl_2\overset{''''}{S}O$ and $\overset{''''}{S}O_2$, and $Cl_2\overset{vi}{S}O_2$ and $\overset{vi}{S}O_3$? Persistency of different equivalent values in double decomposition, as of stannous and stannic salts by lime:

$$Cl_2Sn'' + CaO = Cl_2Ca + Sn''O$$
$$Cl_4Sn'''' + 2CaO = 2Cl_2Ca + Sn''''O_2$$

Theoretical views concerning change of equivalency, real or apparent. Hypo- and hyper- saturated compounds. Saturation by one another of two equivalencies of same atom (?).

(6.) Acids and Salts.

Bodies of which the hydrogen is easily replaced by metal classed as acids. Binary acids exemplified by hydrochloric acid HCl; ternary, by nitric acid HNO_3, and sulphuric acid H_2SO_4, &c. Displacement of hydrogen by metal of caustic alkali, with production of water, the conventional criterion of acidity:

$$HCl + NaHO = NaCl + H_2O$$
$$HNO_3 + KHO = KNO_3 + H_2O$$

Bodies obtainable from acids, by replacement of metal for hydrogen, classed as salts. Action of acids on salts, as of sulphuric acid on nitre, to form new acids and new salts, by exchange of metal for hydrogen:

$$KNO_3 + H_2SO_4 = HNO_3 + KHSO_4$$

Conventional notion of relative power of acids derived from their liberation of one another, as above, by exchange of metal of

salt for hydrogen of stronger acid. Effect of acids on litmus-paper, due to setting free of feeble litmus-acid. Principal di-, tri-, and tetra-oxygen acids:

HBO_2	Boric				
HNO_2	Nitrous	HNO_3	Nitric		
$HClO_2$	Chlorous	$HClO_3$	Chloric	$HClO_4$	Perchloric
H_2CO_2	Formic	H_2CO_3	Carbonic	$H_2C_2O_4$	Oxalic
H_2SO_2	Hyposulph.	H_2SO_3	Sulphurous	H_2SO_4	Sulphuric
H_3PO_2	Hypophosp.	H_3PO_3	Phosphorous	H_3PO_4	Phosphoric

Use of the suffixes *ous* and *ic*, corresponding to *ite* and *ate*; and of the affixes *hypo* and *per*.

Distinction between mono- and poly-basic acids, according to displaceability by metal of one or more atoms of hydrogen. Degree of basicity not necessarily determined by mere number of hydrogen atoms. The nitrous HNO_2, formic H_2CO_2, and hypophosphorous H_3PO_2, acids, alike monobasic, or capable of having but one atom of hydrogen replaced as above by metal.

Conventional representation of dibasic acids and salts as compounds of basylous and stylous oxide, exemplified by sulphates and carbonates. Non-acid properties of the stylous oxides or anhydrides. Alternative use of both forms of expression:

H_2SO_4	or	$H_2O.SO_3$	H_2CO_3	or	$H_2O.CO_2$
$KHSO_4$	,,	$KHO.SO_3$	$KHCO_3$	,,	$KHO.CO_2$
K_2SO_4	,,	$K_2O.SO_3$	K_2CO_3	,,	$K_2O.CO_2$
$Ca''SO_4$	,,	$Ca''O.SO_3$	$Ca''CO_3$	,,	$Ca''O.CO_2$

Active or feeble combination of different anhydrides with water, to form acids. Effervescence of carbanhydride produced by action of acids on carbonates, as of hydrochloric acid on chalk, a test of acidity:

$$2HCl + Ca''CO_3 \text{ or } CaO.CO_2 = Cl_2Ca + H_2O + CO_2$$

Impossibility of representing single molecules of mono- and tri-basic acids as compounds of water and anhydride. Anhydrides of these acids derivable from, or transformable into, two atoms of acid:

$$H_2O + N_2O_5 = 2HNO_3$$
$$3H_2O + P_2O_5 = 2H_3PO_4$$

Necessarily complex formulæ of diad salts of mono- and tribasic acids, as $\overset{''}{Ba}(NO_3)_2$, and $\overset{''}{Ca}_3(PO_4)_2$, nitrate of barium and phosphate of calcium respectively. Their alternative representation as compounds of base and anhydride, thus $BaO.N_2O_5$, and $3CaO.P_2O_5$.

Various modes of formulating the same compound, as sulphuric acid H_2SO_4, deducible from its various decompositions. Action of zinc Zn, to set free hydrogen H_2; of magnesia MgO, to set free water H_2O; of peroxide of barium BaO_2, to set free peroxide of hydrogen H_2O_2; and of sulphide of iron FeS, to set free sulphide of hydrogen H_2S. Consequent representation of sulphuric acid by respective composite formulæ, $H_2.SO_4$, $H_2O.SO_3$, $H_2O_2.SO_2$ and $H_2S.O_4$. Above formulæ also warranted by electrolysis of the acid, and its various modes of recomposition. Use of formula $H_2O_2.SO_2$ or $(HO)_2SO_2$, and its analogues, very general.

Occasional representation of basic hydrylates as compounds of water and basic oxide. Representation of slaked lime for instance as $CaO.H_2O$, instead of $Ca(HO)_2$ or CaH_2O_2; and of caustic potash as $K_2O.H_2O$, instead of 2KHO. Convenient substitution of expression K_2O for 2KHO, in equations where H_2O is eliminated. Action of nitric peroxide on caustic potash for instance,

$$2KHO + 2NO_2 = H_2O + KNO_3 + KNO_2$$

expressible conventionally by simpler equation:

$$K_2O + 2NO_2 = KNO_3 + KNO_2$$

(7.) Formula of Water.

Specific heats of 1 part by weight of hydrogen, of 35·5 parts by weight of chlorine (nearly), of 16 parts of oxygen, and of 14 parts of nitrogen found to be the same. Hence only with the atomic weight 16, does oxygen have the same atomic heat as the other three elementary gases.

The volumes of 1 part by weight of hydrogen, of 35·5 parts by weight of chlorine, of 16 parts by weight of oxygen, and of

14 parts by weight of nitrogen found to be the same. Hence only with the atomic weight 16, does oxygen have the same atomic volume as the other three elementary gases.

The proportion of constituent oxygen in well defined molecules always found to be 16 parts, or some multiple of 16 parts. Hence only with the atomic weight 16, can oxides be represented to contain or differ from one another by a single atom of oxygen, as in oxides of potassium-chloride for instance, KCl, KClO, $KClO_2$, $KClO_3$, $KClO_4$.

Equal volumes of chlorine, oxygen, and nitrogen found to combine with 1, 2, and 3 volumes of hydrogen respectively. Hence representation of water with two atoms of hydrogen H_2O, consequent upon the representation of hydrochloric acid with one atom HCl, and of ammonia with three atoms H_3N.

Volume of $1+35{\cdot}5$ parts by weight of hydrochloric acid, of $2+16$ parts of steam, and of $3+14$ parts of ammonia, found to be the same, and double that of 1 part by weight of hydrogen. Hence only with the formula H_2O, and molecular weight 18, does water correspond to the same 2-volume formula as hydrochloric acid HCl, and ammonia H_3N.

In cases of definite decomposition, the proportion of reacting or resulting water always found to be 18 parts, or some multiple of 18 parts; and among bodies differing in their amounts of constituent water, the excess or deficit of water always found to be 18 parts, or some multiple of 18 parts. Hence 18 parts the atomic proportion of water, or least indivisible proportion of water entering into or liberated from a combination.

Displacement of the hydrogen of ammonia in thirds at three successive stages, that of the hydrogen of water in halves at two successive stages, and that of the hydrogen of hydrochloric acid at once or not at all. Hence representation of dipartite hydrogen of water in formula H_2O, consequent upon representation of atomic hydrogen of hydrochloric acid in formula HCl, and of tripartite hydrogen of ammonia in formula H_3N.

(8.) Heat of Combination.

Quantity of heat evolved by same chemical action, whether rapid or slow, invariable. Temperature, or intensity of heat, variable, dependent upon rapidity of action, and upon amount and kind of matter heated. Correlative increase in rapidity of action by increase of temperature. For above reasons, intensities of heat different in combustions of same body in oxygen and air respectively. Nature of slow combustion or eremacausis. Spontaneous combustion brought about by gradual increase in chemical action, consequent upon increase of temperature due to chemical action, and so on. Animal heat a result of eremacausis.

Evolution of 24, 50, and 30 units of heat respectively, by combination of 1 gramme of hydrogen, 32·5 grammes of zinc, and 31·75 grammes of copper with 35·5 grammes of chlorine, to form gaseous hydrochloric acid, and solid chorides of zinc and copper respectively.

Evolution of 34, 24, 42, and 19 units of heat respectively, by combination of 1 gramme of hydrogen, 3 grammes of carbon, 32·5 grammes of zinc, and 31·75 grammes of copper, with 8 grammes of oxygen, to form liquid water, gaseous carbanhydride, and solid oxides of zinc and copper respectively.

Observed evolution of 34 units of heat by combustion of 1 gramme of hydrogen with 8 grammes of oxygen, due to latent heat of vaporisation of 9 grammes of water, say 5·5 units, in addition to actual heat of combination, or 28·5 (=34−5·5) units. Analogous corrections necessary, though seldom practicable, in most other instances.

Amounts of heat evolved by equal increments of oxidation sensibly equal. Evolution, for example, of 9·5 × 2 or 19 units of heat by combustion of 31·75 grammes of solid copper with 8 grammes of oxygen; and of 9 units of heat by combustion of 31·75 + 4 grammes of solid cuprous oxide with 4 grammes of oxygen. But evolution of only 24 units of heat by combustion

of 3 grammes of solid carbon with 8 grammes of oxygen; and of 17 units of heat by combustion of $3+4$ grammes of gaseous carbonic oxide with 4 grammes of oxygen. Consequent absorption of 10, or twice $17-24$, units of heat in vaporisation of carbon (?).

Calorimetric effect of any change equal and opposite to that of its reversal, instanced by absorption of 34 units of heat in decomposition or unburning of 9 grammes of water. With necessary correction for changes of physical state, combustion-heat of compounds less than that of their separate constituents by quantity of heat absorbed in decomposition of the compounds.

Heat evolved by solution of metallic zinc in salts of hydrogen, copper, &c., the difference between + heat of burning zinc, and − heat of unburning hydrogen or copper. Combustion of zinc effected in cell of galvanic battery. Heat manifested at a distance in ignition of platinum wire, charcoal points, &c., or rendered latent in electrolytically separated oxygen and hydrogen gases, and liberable by their recombination.

Potential energy of free oxygen and hydrogen gases, gunpowder, gun-cotton, &c., compared with potential mechanical energy of raised weight, stretched cross-bow, &c. Strength of chemical affinity between any two bodies measured by quantity of heat required to separate them from, or evolved by their combination with, each other.

Potential energy of zinc and other metals derivable from potential energy of carbon. Potential energy of carbon traceable to the sun. Absorption of sun's heat in separation of carbon and oxygen from one another in organism of growing plant.

Unit of heat equivalent to motion of 1 kilogramme weight through height of 424 metres, *i.e.* to 424 kilogrammetres of motion. Combustion-heat of 1 gramme of hydrogen equal to $34 \times 424 = 14416$ kilogrammetres; and that of 1 gramme of carbon equal to 8×424 or 3392 kilogrammetres of motion.

CHAPTER II.

(9.) HYDROGEN.

SYMBOL, H; atomic weight, 1. Its abundant existence in the form of water. Also in inflammable minerals such as coal. Its occurrence as a constituent of all animal and vegetable tissues, especially of fat. Likewise of various alkalis, neutral bodies, and all acids whatsoever.

Its liberation by the action of sodium or zinc on hydrochloric or sulphuric acid, at ordinary temperatures; with exchange of metal for the hydrogen of chloride and sulphate of hydrogen respectively:

$$2HCl + Na_2 = 2NaCl + H_2$$
$$H_2SO_4 + Zn'' = Zn''SO_4 + H_2$$

Its production by the action of charcoal, iron, &c., upon oxide of hydrogen or steam at a red heat:

$$H_2O + C = CO + H_2$$
$$4H_2O + Fe_3 = Fe_3O_4 + H_8$$

Also from potash KHO, or soda NaHO; and by many reactions of organic bodies.

Construction of gas-generating apparatus. Collection of hydrogen over pneumatic trough.

Properties of hydrogen gas. Its extreme lightness, whence its specific gravity chosen as unity, that of air being 14·47. Its capability of collection and transference from one vessel to another by displacement of air. Its high diffusibility. Its incondensability and practical insolubility.

Inflammability of hydrogen in air. Production of water by its combustion. Different modes of burning hydrogen and air together. Chemical action limited to surfaces in contact. Little light and great heat of hydrogen flame.

General inertness of free hydrogen. Its combination with free chlorine in daylight, and with free oxygen by aid of spongy platinum. Reducing action of hydrogen at a red heat, or in nascent state, upon metallic and other compounds:

$$Cu''O + H_2 = H_2O + Cu$$

Direct or indirect substitutions of either chlorine or metal for the hydrogen of various compounds, illustrated by marsh-gas or methene H_4C, chloromethene ClH_3C, and sodio-methene NaH_3C, &c. General nature of acids or salts of hydrogen,—those hydrogenised bodies in which metal-substitution is most readily effected. Quasi-metallic characters of hydrogen.

(10.) Halogen Elements.

Fluorine—Chlorine, Bromine, and Iodine.

Their common property of combining with hydrogen in the proportion of gaseous volume to gaseous volume, or atom to atom. The respective combinations unattended by condensation. The products all powerful acids, gaseous, soluble in water, and obtainable by similar reactions. Atomic weights and symbols:

F	Fluorine	19	
Cl	Chlorine	35·5	} 80·8 mean.
Br	Bromine	80	
I	Iodine	127	

Special characters of fluorine. Gradational differences of other three elements. Expulsion of iodine from iodides by bromine, and of bromine from bromides by chlorine.

(11.) Chlorine—Bromine—Iodine.

Their principal occurrence in the forms of chloride, bromide, and iodide of sodium, &c., in sea-salt or rock-salt, in residues of sea- and certain mineral waters, and in ash of sea-weed respectively.

Manufacture of **chlorine** by action of peroxide of manganese upon chloride of hydrogen :

$$MnO_2 \ + \ 4HCl \ = \ 2H_2O \ + \ \overbrace{Mn''Cl_2 \ + \ Cl_2};$$

or upon a mixture of sulphuric acid and chloride of sodium :

$$MnO_2 + 2H_2SO_4 + 2NaCl = 2H_2O + Na_2SO_4 + Mn''SO_4 + Cl_2$$

Relationship of two processes. Intermediate production and subsequent dehydrogenation of hydrochloric acid :

$$\begin{array}{lllllllllll} & & H_2SO_4 & + & 2NaCl & = & & & Na_2SO_4 & + & 2\mathit{HCl} \\ MnO_2 & + & H_2SO_4 & + & 2\mathit{HCl} & = & 2H_2O & + & Mn''SO_4 & + & Cl_2 \end{array}$$

Use of other oxygenants or dehydrogenants instead of peroxide of manganese. Collection of chlorine gas over warm water in pneumatic trough, or by downward displacement.

Similar processes for obtaining **bromine** and **iodine**. Previous preparation of requisite bromides and iodides from mother-liquors of sea-salt and sea-weed-ash respectively. Bromine liberated by chlorine, taken up by ether, and fixed by potash or soda:

$$2NaBr \ + \ Cl_2 \ = \ 2NaCl \ + \ Br_2$$

Comparison of the three elements. Their usual states of aggregation, gaseous, liquid, and solid respectively. Boiling point of bromine 63°, of iodine 175°. Alike coloured, corrosive, irrespirable, and very heavy gases. Sequence of vapour-densities, 35·5, 80, and 127. Liquefaction of chlorine by cold or pressure, and solidification of bromine. Specific gravities of liquid chlorine and bromine 1·33, and 2·97, of solid iodine 4·95.

Solubility of the three elements in different menstrua. Solution in one volume of water of 2·4 volumes of chlorine. Definite solid hydrates of chlorine $Cl_2.10H_2O$, and of bromine $Br_2.10H_2O$, at 0°. Instability of chlorine solutions, especially in sunlight. Effect of iodide of potassium upon solubility of iodine. Colour of iodine solutions in ether, alcohol, chloroform, disulphide of carbon, &c. Action of iodine and bromine upon starch.

Incombustibility of all three elements in air or oxygen. Com-

bustibility of chlorine and hydrogen, the one in or with the other. Rapid combination of halogens with metals or pseudo-metals, as copper, arsenic, phosphorus, &c. Action of chlorine on alkalis to form hypochlorite and chloride:

$$K_2O \;+\; Cl_2 \;=\; KClO \;+\; KCl$$

Similar actions of bromine and iodine.

Consecutive displacements of iodine, bromine, and chlorine by one another. Their displacements of hydrogen in various bodies, with production of hydracid. Action of chlorine on marsh-gas *for instance:*

$$H_4C \;+\; Cl_2 \;=\; ClH_3C \;+\; HCl$$

Qualification as regards iodine. Resemblance between original bodies and their halogen derivatives. Acid character of bodies intensified and basic character reduced by chlorine substitution.

Violent combination of halogens with the hydrogen of certain hydrides as of sulphur, nitrogen, carbon, &c. Indirect action of halogens as oxygenants, in presence of moisture:

$$H_2O \;+\; Cl_2 \;=\; 2HCl \;+\; O$$

Action of chlorine as a bleaching, deodorising and disinfecting agent, dependent on its affinity for hydrogen, and indirect oxygenation.

(12.) Halogen Hydracids.

Production of hydrochloric acid, HCl or ClH, by direct union of hydrogen and chlorine. Also by reaction

(α.) of hydrides, as sulphuretted hydrogen, upon chlorine:

$$H_2S \;+\; Cl_2 \;=\; S \;+\; 2HCl;$$

(β.) of sulphuric or other strong acid on basylous chlorides, as chloride of sodium:

$$H_2SO_4 \;+\; NaCl \;=\; NaHSO_4 \;+\; HCl;$$

(γ.) of water, &c., on acid-chlorides, as chloride of phosphorus:

$$4H_2O \;+\; Cl_5P \;=\; H_3PO_4 \;+\; 5HCl$$

Hydrochloric acid gas usually made by action of sulphuric acid on fused common salt, and collected over mercurial trough, or by downward displacement.

Hydrobromic and hydro-iodic acids, HBr and HI, producible by similar reactions. Use of phosphoric instead of sulphuric acid in process β. Production of hydro-iodic acid from phosphorus, iodine, water, and iodide of potassium, or by processes γ and β jointly.

Properties of hydrochloric acid gas. Its specific gravity $\frac{1+35 \cdot 5}{2} = 18 \cdot 25$. Its liquefaction by cold and pressure. Its hygroscopicity, shown by its fuming in air. Solution in one volume of water at 15°, of 458 volumes of hydrochloric acid. Its absorption by ammonia to form sal-ammoniac. Its incombustibility.

Similar properties of hydro-bromic and hydro-iodic acid gases. Action of oxygenants on hydro-iodic acid. Its instability:

$$2HI + O = H_2O + I_2$$

Manufacture of aqueous hydrochloric acid, by condensing the gas in water. Bulk of condensing liquid increased threefold. Gas produced from two atoms of salt:

$$\begin{aligned} H_2SO_4 + 2NaCl &= NaHSO_4 + NaCl + HCl \\ &= Na_2SO_4 + 2HCl \end{aligned}$$

Reaction effected at two stages, with intermediate production of hydro-sodium sulphate $NaHSO_4$. Composition of acid of 1·21 specific gravity, $HCl.3H_2O$. Composition of ordinary acid, $HCl.4H_2O$. Its specific gravity 1·162. Composition of acid of constant boiling point, about $HCl.8H_2O$. Its specific gravity 1·11. Evolution of hydrochloric acid gas from stronger solutions when heated. Their property of fuming in air, especially when ammoniacal.

Acidity of ordinary and more dilute solutions, shown by their reddening litmus and effervescing with carbonates. Action of aqueous acid on sodium, zinc, iron, &c., accompanied by evolution of hydrogen:

$$Zn + 2HCl = H_2 + Cl_2Zn''$$

Its want of action on copper (?), silver, and mercury. Its solution of metallic oxides with liberation of water, and of peroxides with liberation of water and chlorine:

$$CuO + 2HCl = H_2O + Cl_2Cu$$
$$MnO_2 + 4HCl = 2H_2O + Cl_2Mn + Cl_2$$

Similar properties of aqueous hydrobromic acid. Instability of aqueous hydro-iodic acid. Its employment in organic chemistry as a hydrogenising agent, instanced by its action on kinone:

$$H_4C_6O_2 + 2HI = H_6C_6O_2 + I_2$$

Destruction of blue iodide of starch by sulphurous acid and all reducing agents, through conversion of iodine into hydro-iodic acid:

$$H_2SO_3 + H_2O + I_2 = H_2SO_4 + 2HI$$

Restoration of blue colour by oxygenants through reproduction of free iodine:

$$HClO + 2HI = HCl + H_2O + I_2$$

Hydrogenation of free iodine by reducing, and dehydrogenation of hydro-iodic acid by oxidising agents, the basis of Bunsen's general method of volumetric analysis.

Proofs of the composition of hydrochloric acid gas. Its decomposition by sodium with evolution of hydrogen. Its decomposition by peroxide of manganese with evolution of chlorine. Production of equal volumes of chlorine and hydrogen gases by its electrolysis. Existence in two volumes of hydrochloric acid gas of one volume of hydrogen, and consequently of one volume of chlorine, shown by action of sodium-amalgam. Synthetic experiments. Correspondence of the molecule of hydrochloric acid gas to two units of volume also shown by its specific gravity 18·25, being the half of its atomic weight. Similar conclusions with regard to hydrobromic and hydro-iodic acid gases.

Equal bulks of hydrogen, hydrochloric acid, and chlorine, expressed by the symbols HH, HCl, and ClCl, respectively. Re-

presentation by these formulæ of comparable 2-volume molecules of the three bodies, or quantities which in their reactions correspond with and are equivalent to one another. Distinction between atoms and molecules. Reasons for believing that in each of the three molecules H_2, HCl, and Cl_2 the two constituent atoms are similarly combined with each other. Action of hydroiodic acid on iodo-derivatives, as iod-acetic acid:

$$IH_3C_2O_2 + HI = H_4C_2O_2 + I_2$$

(13.) Halogen Oxacids and Salts.

Acids		Salts
HCl	Hydrochloric	KCl
HClO	Hypochlorous	KClO
$HClO_2$	Chlorous	$KClO_2$
$HClO_3$	Chloric	$KClO_3$
$HClO_4$	Perchloric	$KClO_4$

Direct oxidation of hydrochloric into hypochlorous acid. Chloric acid $HClO_3$, producible by metamorphosis of hypochlorous acid HClO; reducible into chlorous acid $HClO_2$; oxidisable and otherwise transformable into perchloric acid $HClO_4$.

Mutual relations of water H_2O, hypochlorous acid HClO, hypochlorous oxide Cl_2O, potassium-hypochlorite KClO, hydrylate KHO, and oxide K_2O.

HYPOCHLOROUS COMPOUNDS.

Hypochlorous oxide or anhydride Cl_2O, a yellow, heavy, very unstable vapour, made by passing chlorine over precipitated and dry red oxide of mercury:

$$HgO + Cl_4 = Cl_2O + Cl_2Hg$$

Combination of resulting chloride with excess of oxide of mercury, to form insoluble oxichloride Cl_2Hg_2O.

Hypochlorous acid HClO, producible by reaction of anhydride with water:

$$H_2O + Cl_2O = 2HClO$$

Its solution made by passing chlorine gas through water in which oxide of mercury or chalk is suspended, and filtering or distilling:

$$H_2O + HgO + Cl_4 = 2HClO + Cl_2Hg$$
$$H_2O + CaO.CO_2 + Cl_4 = 2HClO + Cl_2Ca + CO_2$$

A volatile, feebly acid, strongly bleaching, oxidising, and chlorinating liquid. Its transformation into chloric acid. Its decomposition by silver-oxide with evolution of oxygen, and by strong hydrochloric acid with evolution of chlorine:

$$HClO + HCl = H_2O + Cl_2$$

Reverse action of chlorine on water and alkalis.

Hypochlorites produced in pure state by neutralising hypochlorous acid with caustic alkali. Bleaching salts of commerce (mixtures or compounds of hypochlorite and chloride) made by passing chlorine through solution of caustic or carbonated alkali, or over hydrated alkaline earth:

$$2NaHO + Cl_2 = H_2O + NaClO \quad NaCl$$
$$CaH_2O_2 + Cl_2 = H_2O + Ca''\begin{cases} ClO \\ Cl \end{cases}$$

Liberation, from the commercial salts, of hypochlorous acid by a slight, and of chlorine by an excessive acidulation. Different bleaching action of their solutions before and after acidification. Their employment as precipitants of metallic peroxides, and as sources of oxygen. Their catalytic decomposition by cobalt-oxide:

$$CaCl_2O = CaCl_2 + O$$

CHLOROUS COMPOUNDS.

Chlorous anhydride Cl_2O_3, a yellow unstable gas, produced by reduction of chloric acid with nascent nitrous anhydride. **Chlorous acid** $HClO_2$, an ill-defined, feebly acid, strongly bleaching compound, formed by solution of anhydride in water:

$$H_2O + Cl_2O_3 = 2HClO_2$$

Chlorites. Alkali- &c.- salts soluble, made by neutralising acid. Heavy metal-salts insoluble, precipitable by double decomposition.

CHLORIC COMPOUNDS.

Chloric acid $HClO_3$, liberated by action of fluosilicic acid on potassium-salt, or of dilute sulphuric acid on barium-salt. Its anhydride Cl_2O_5, unknown. Oxidising and bleaching properties of chloric acid and its solutions. Its reduction by sulphurous acid. Its instability, and decomposition into perchloric acid and the elements of chlorous acid:

$$2HClO_3 = HClO_4 + HClO_2(?)$$

Chlorates. That of potassium produced by action of chlorine on dissolved caustic or carbonated potash. Reaction effected at two stages. Formation of hypochlorite, and its decomposition by ebullition into chlorate and chloride:

$$\begin{aligned} 6KHO + Cl_6 &= 3H_2O + 3KClO + 3KCl \\ &= 3H_2O + KClO_3 + 5KCl \end{aligned}$$

Purification of chlorate by crystallisation. Its manufacture from mixture of carbonate of potassium and slaked lime, with co-production of chloride of calcium.

Final action of heat on chlorate of potassium to leave chloride, but on chlorate of magnesium to leave oxide:

$$KClO_3 = KCl + O_3$$

Use of chlorate of potassium as a deflagrating agent.

Action of strong sulphuric acid on chlorate of potassium to form chloric peroxide ClO_2 or Cl_2O_4, and perchlorate of potassium $KClO_4$. Evolution of Cl_2 plus O_4 by nitric acid.

Chloric peroxide, a brownish-yellow, unstable, very explosive gas. Spontaneous combustion in it of phosphorus, sugar, ether, &c. Its decomposition by alkalies into chlorite and chlorate:

$$K_2O + Cl_2O_4 = KClO_3 + KClO_2$$

Action of hydrochloric acid on chlorate of potassium to form euchlorine—a mixture of chlorine and chloric peroxide in proportion to form hypochlorous oxide:

$$Cl_2 \quad + \quad 3ClO_2 \quad = \quad 6Cl_2O.$$

PERCHLORIC COMPOUNDS.

Perchloric acid $HClO_4$, made by treating perchlorate of potassium with sulphuric acid, or by distilling chloric acid:

$$4HClO_3 \quad = \quad 2HClO_4 \quad + \quad 2\mathit{HClO_2} \quad (\text{or } H_2O + Cl_2 + O_3)$$

Acid rendered absolute by distillation off oil of vitriol. Oily, unstable, explosive liquid. Existence of decomposible crystalline hydrate $HClO_4.H_2O$, and volatile oily hydrate $HClO_4.2H_2O$. Solutions of the acid very stable, and devoid of bleaching properties. The anhydride Cl_2O_7, unknown.

Perchlorates. That of potassium made by heating the chlorate, so as to expel one-third of its oxygen:

$$2KClO_3 \quad = \quad KClO_4 \quad + \quad \mathit{KClO_2} \; (\text{or } KCl + O_2);$$

or by acting on it with nitric or sulphuric acid.

The perchlorates, sparingly soluble deflagrating salts, distinguished from the chlorates by their indifference to nitric, sulphuric and hydrochloric acid.

Analogous oxi-compounds of bromine and iodine. Bromate of potassium made with pentachloride of bromine:

$$6KHO \quad + \quad Cl_5Br \quad = \quad 3H_2O \quad + \quad KBrO_3 \quad + \quad 5KCl.$$

Iodate of potassium made by similar process, or by action of iodine on the acidified chlorate. Iodic acid HIO_3, made by oxidising iodine with nitric acid. Its use as a test for reducing agents such as sulphurous acid and morphia:

$$5H_2SO_3 \quad + \quad 2HIO_3 \quad = \quad 5H_2SO_4 \quad + \quad H_2O \quad + \quad I_2$$

Periodates, as KIO_4, made by passing chlorine through solutions of

iodate in alkali. Existence of iodic and periodic (?) anhydrides, I_2O_5 and I_2O_7.

(14.) Fluorine.

Its principal sources, fluor-spar or fluoride of calcium F_2Ca, and cryolite or double fluoride of aluminium and sodium Na_3F_6Al. Traces of fluorine very widely distributed in mineral, vegetable, and animal kingdoms, particularly in bones, recent and fossil. Apparent isolation of fluorine by action of dry iodine on fluoride of silver, and in other ways:

$$2AgF + I_2 = 2AgI + F_2$$

A colourless gas having the general chemical properties of chlorine in an intensified degree, and a remarkable power, unless absolutely dry, of attacking glass and silicated compounds, probably through formation of hydrofluoric acid:

$$H_2O + F_2 = 2HF + O$$

Hydrofluoric acid gas HF, best obtained anhydrous by heating the double fluoride of potassium and hydrogen KF.HF. Ordinarily procured from fluoride of calcium, much as hydrochloric acid is from chloride of sodium, by treatment with sulphuric acid. Reaction effected in leaden retorts:

$$H_2SO_4 + F_2Ca = Ca''SO_4 + 2HF$$

An incombustible, colourless, strongly acid, and easily condensable gas, soluble in water and fuming in moist or ammoniacal air.

Aqueous hydrofluoric acid, a colourless, strongly acid, corrosive, fuming liquid, usually kept in vessels of lead or gutta percha. Specific gravity of most concentrated acid 1·06. The acid of constant boiling point and greatest density, 1·15, a dihydrate, $HF.2H_2O$. Action of hydrofluoric acid on basylous metals and metallic oxides similar to that of hydrochloric acid.

Processes of etching on glass with hydrofluoric acid gas, or its solution in water:

$$4HF + SiO_2 = F_4Si + 2H_2O$$

(15.) Monad Metals and Chlorides, &c.

Potassium, rubidium, and cæsium, the correlatives of the halogen elements. Their differences strictly gradational. Sodium unlike potassium in various particulars, and lithium still more unlike. Special characters of silver.

Atomic weights and symbols:

Li	Lithium	7
Na	Sodium	23
K	Potassium	39
Rb	Rubidium	85
Cæ	Cæsium	133
Ag	Silver	108

Solubility in water of chlorides of alkali-metals, NaCl, KCl, &c., and of their fluorides, bromides, and iodides. Soluble chlorides made by dissolving carbonates in hydrochloric acid. Those of sodium and potassium found native. Bromides and iodides made by saturating basylous hydrate with halogen, and igniting to expel oxygen from bromate or iodate:

$$6KHO + I_6 = 3H_2O + KIO_3 + 5KI;$$

or from ferrous halide by decomposition with alkaline carbonate. Salts readily with fusible and, at a high temperature, volatile.

Chloride of silver AgCl, and corresponding bromide and iodide, insoluble fusible compounds, thrown down as clotty precipitates on adding dissolved chloride, bromide, or iodide of metal or hydrogen to solution of any silver salt:

$$AgNO_3 + NaCl = NaNO_3 + AgCl$$

The several halides distinguishable from all other silver precipitates by their insolubility in boiling nitric acid. Distinguish-

able from one another by difference in colour and solubility in ammonia. Fluoride of silver AgF, a readily soluble salt. Association of silver with sodium and alkali-metals.

Inferior chlorides, &c., of thallium, gold, copper, and mercury referrible to the formula MCl or M_2Cl_2. Their general resemblance to chloride of silver.

Double salts such as KF.HF, NaCl.AgCl, KI.AgI, &c. formed by combination of monad halides. Comparative stability of double fluorides of hydrogen and metal. Instability of other compounds.

Of chlorous monochlorides, those of hydrogen HCl, and chlorine ClCl, preconsidered. Chloride of fluorine unknown. Monochlorides of bromine and iodine, red or brown liquids, not satisfactorily isolable, made by acting on bromine and iodine with chlorine.

Atomic heats of monad elements, halogenous and metallic, represented approximately by the number 6·2. Atomic heats of metallic monochlorides expressed by the number 12·4. Derivation of these numbers from the specific heat of 1 part by weight of water taken as unity.

NOTE.—Gas-volume of 1 gramme of hydrogen, 35·5 grammes of chlorine, 16 grammes of oxygen, 14 grammes of nitrogen, &c. &c., measured at 760 mm., and 0° C., 11·2 litres (11·19).

Or, at same pressure, weight of 1 litre of hydrogen at temperature of − 30°, 1 decigramme; and at temperature of 0°, 1 crith, or ·09 gramme (·0893).

OXYGEN—Sulphur, Selenium, Tellurium.

Their property of combining with hydrogen in the proportion of one volume to two. Production of neutral or but faintly acid compounds. Their symbols and atomic weights:

O	Oxygen	16	
S	Sulphur	32	80 mean.
Se	Selenium	79	
Te	Tellurium	129	

Special characters and interest of oxygen. Strictly gradational characters of sulphur, selenium, and tellurium. Semi-metallic nature of tellurium. General increase of metallic character with increase of atomic weight in members of the same electro-negative group. Comparison of halogen and oxygen elements.

(17.) OXYGEN.

Its great abundance and varied distribution in nature so as to constitute about $\frac{1}{2}$ of the earth's crust. Its proportion in water $\frac{8}{9}$, in air nearly $\frac{1}{4}$, and in clay, sand, and limestones about $\frac{1}{2}$. Its existence in most important minerals, and in all organic tissues.

a. Its liberation by the action of heat upon oxide of mercury, peroxide of barium, peroxide of manganese, sulphuric acid, bleaching powder, nitre, and especially chlorate of potassium, admixed or not with some heavy metallic oxide:

$$HgO = Hg + O$$
$$3MnO_2 = Mn_3O_4 + O_2$$
$$KClO_3 = KCl + O$$

Absorption of oxygen from the atmosphere by means of mercury, baryta, sulphurous acid, &c., and its separation from resulting compounds by an increase of heat.

β. Liberation of oxygen by action of sulphuric acid upon peroxide of manganese, red chromate of potassium, and other highly oxidised bodies:

$$H_2SO_4 + MnO_2 = Mn''SO_4 + H_2O + O$$

γ. Its evolution from carbanhydride and water, by action of growing vegetables in sunlight; and its production by miscellaneous reactions.

Low refrangibility, paramagnetism, incondensability, and sparing solubility of oxygen. Its specific gravity of 16, greater than that of air in the ratio of 11 to 10 nearly. Its existence in the air in an uncombined state. Its action upon phosphorus, nitric oxide, pyrogallic acid, &c. at ordinary temperatures, whereby its presence in gaseous mixtures recognisable. Feeble action of dry oxygen upon metals in massive state. Pyrophoric lead, iron, &c. Rusting of metals in moist air.

Its action on ignited combustibles to increase the rapidity of their burning. Its property of re-inflaming a glowing taper or splinter of wood, and of maintaining the brilliant combustion of charcoal, resin, coal-gas, &c. Combustion of metallic iron and zinc in oxygen, of magnesium in air, &c.

Acidifying property of oxygen, whence its name. Converse production of bases by oxidation, and existence of non-oxidised acids. With same hydrogenised grouping, extent of acid character proportional to degree of oxidation. Illustration furnished by the monobasic, dibasic, and tribasic oxides of phosphoretted hydrogen H_3PO_2, H_3PO_3, and H_3PO_4. Substitutions of oxygen for hydrogen and chlorine. The atom of oxygen di-valent.

Ozone a modification of oxygen having a peculiar smell and exalted chemical activity, shown especially by its setting free iodine from iodide of potassium, and oxidising mercury. Early observations of Van Marum, Schönbein, and others. Production

of ozone from dry oxygen. Complete *pari passu* absorption of electrised oxygen by iodide of potassium solution. Complete decomposition of ozone by heat of 290°.

Principal modes of producing ozone. By transmission of silent electrical discharges through oxygen or air. By electrolysis of acidulous or saline solutions. By oxidation of moist phosphorus, ether, &c.

Constitution of ozone. Representation of its molecule by the symbol O_3 or O_2O. Andrew's experiments on condensation or ozonification of oxygen by silent electrical discharges, and its re-expansion by heat. Absorption of the condensed oxygen by mercury and iodide of potassium solution, released from glass bulbs. Quantity of iodine set free equivalent to quantity of oxygen condensed. Complete absorption of ozone by turpentine.

General action of ozone as an oxygenant. Its special reducing action, as on peroxide of hydrogen:

$$H_2OO + O_2O = H_2O + O_2 + O_2$$

Its unlimited decomposition by certain metals and oxides, as silver and peroxide of manganese. Probable series of oxidations and reductions. Atmospheric ozone.

(18.) Water.

Hydric oxide or protoxide of hydrogen, H_2O or OH_2. Its abundant existence in nature in solid, liquid, and gaseous states. Its presence in all living tissues, vegetal and animal. Its forming $\frac{7}{8}$ of the entire human body.

Constant circulation of water from sea to air, air to rivers, and rivers to sea. Varieties of natural water. Rain water and melted ice the purest varieties. Water artificially purified by distillation, with requisite precautions. Its redistillation off fixed acids and alkalis.

Physical properties of water. Its appearance, elasticity, and non-conductivity. Its great specific heat, taken as unity. Heat of summer stored up in water of the ocean and restored to the

atmosphere in winter. Specific heat of 1 volume of water equal to that of 3234 volumes of air. Density of water taken as the standard of specific gravity. Weight of 1 cubic centimetre of water at 4° C., 1 gramme. Weight of 1 cubic inch at 60° F., 252·456 grains.

Solidification of water into ice at 0°. Point of maximum density at 4°, shown by Hope's experiment. Of two thermometers suspended respectively at top and bottom of jar of cooling water, the lower one first affected down to 4°, and the upper one first affected from 4° to 0°. Consequences of this peculiarity of water. Expansion of water in freezing. Specific gravity of ice 0·94. Heat of liquidity. Freezing mixtures. Latent heat of water evolved during freezing and absorbed during melting. Absorption of 80 units of heat in liquefaction of 1 kilo. of ice. Hence reduction of the temperature of a kilo. of water, from 80° to 0°, in transforming a kilo. of ice at 0° to a kilo. of water at 0°. Meteorological results of latent heat of water. Constancy of melting point. Possibility of cooling liquid water below its ordinary freezing point. Rise of temperature to 0° on solidification. Freezing point lowered by presence of dissolved salts. Separation of pure ice from saline liquids. Crystalline forms of ice. Regelation.

Vaporisation of water at all temperatures, in air or a vacuum. Quantity of vapour existent in given space limited, variable with temperature. Tension of vapour, the elastic force with which it resists compression into the liquid state. Determinate increase in density, and in tension or elastic force, for every successive degree of temperature. Different tensions of different vapours, as of ether, alcohol, water, &c. Occurrence of ebullition, when elastic force of vapour equals atmospheric pressure. Ebullition of water at temperature of 100° C. under pressure of 760 mm., or at 212° F. under pressure of 30 inches, of mercury (29·92). Variability of boiling point with altitude.

Vaporisation of water into 1696 times its volume of steam. Latent heat of steam absorbed during evaporation or ebullition, and evolved during condensation. Absorption of 537 units of

heat in ebullition of 1 kilo. of water. Hence temperature of 5·37 kilos. of water raised from 0° to 100°, by condensation of 1 kilo. of steam at 100° into 1 kilo. of water at 100°.

Constancy of boiling point of water under definite conditions. Effect of dissolved air in producing regularity of ebullition. Boiling point raised by presence of dissolved salts. Spheroïdal state of water.

Composition of water by weight, 88·89% oxygen and 11·11% hydrogen. Its production by union of one volume of oxygen with two volumes of hydrogen, or of 16 parts by weight of oxygen with 2 parts by weight of hydrogen. Specific gravity of steam $\frac{2+16}{2} = 9$. Conversion of three volumes of mixed gas into two volumes of steam, demonstrated also by direct experiment.

Composition of water shown analytically by its electrolysis; and by its transmission over red hot iron (Lavoisier):

$$4H_2O + Fe_3 = Fe_3O_4 + H_8$$

Its composition shown synthetically by combustion of hydrogen in air; by explosion of mixed hydrogen and oxygen in eudiometer; and most accurately by transmission of hydrogen over heated oxide of copper:

$$H_2 + CuO = Cu + H_2O$$

Description of Dumas' experiment with oxide of copper.

Combination of oxygen and hydrogen gases brought about by insolation partially; by sudden pressure; by contact with spongy platinum, &c.; and by ignition. Explosive mixtures. Oxihydrogen blowpipe.

Decomposition of water effected by electrolysis, and intensely heated solids. Action of chlorine in sunlight, or at a red heat, to set free oxygen:

$$H_2O + Cl_2 = 2HCl + O$$

Action of metals and ignited carbon to set free hydrogen:

$$H_2O + C = CO + H_2$$

Liberation of hydrogen by sodium at two successive stages, to form NaHO, and Na_2O. Slow union of phosphorus with both constituents of water.

Reactions of water with electro-negative chlorides to form corresponding acids:

$$3H_2O + Cl_3P = 3HCl + H_3PO_3$$

Its reactions with chlorous and basylous oxides to form acids and alkalis respectively:

$$3H_2O + P_2O_5 = 2H_3PO_4$$
$$H_2O + CaO = H_2CaO_2$$

Direct combinations of water, as such, with acids, alkalis, salts, &c. Difference between water of elimination and water of hydration, illustrated by sulphuric acid and its hydrates. Mutual combination of molecules, as distinguished from that of atoms. Definite hydration of certain compounds, as $CaSO_4$, $CuSO_4$; and indefinite deliquescence of others, whether hydrated as $CaCl_2.2H_2O$, or anhydrous as K_2CO_3.

Existence in many salts of specific number of atoms of water of crystallisation, instanced by $CaSO_4.2H_2O$, $CuSO_4.5H_2O$, $MgSO_4.7H_2O$, &c. Some salts crystallisable with two or more different proportions of water, thus:

$Na_2SO_4.10H_2O$	$Na_2SO_4.8H_2O$
$Na_2HPO_4.12H_2O$	$Na_2HPO_4.7H_2O$
$Na_2B_4O_7.10H_2O$	$Na_2B_4O_7.5H_2O$

Greatest proportion of water in crystals formed from cold dilute solutions. Successive atoms of water retained with different degrees of force, shown by conversion of $MgSO_4.7H_2O$ into $MgSO_4.2H_2O$ by exposure in vacuo over oil of vitriol; into $MgSO_4.H_2O$ by heat of 130°; and into $MgSO_4$ by heat of 210°. The more firmly retained atoms of water in different salts known as constitutional water, and replaceable in certain cases by metallic oxide. Efflorescence of some hydrated salts; as of $Na_2CO_3.10H_2O$ to $Na_2CO_3.5H_2O$, and of $Na_2SO_4.10H_2O$ to anhydrous state. Efflorescence promoted by warmth, dryness, and breaking up of crystals.

Water as a solvent of liquids and solids. Alcohol and water miscible in all proportions. Water and ether miscible to a small extent only. Quantity of any salt dissolved in water always limited, and under fixed conditions special for each salt. Solution of $\frac{1}{700}$ part of calcium- and of $\frac{1}{3}$ part of magnesium-sulphate in 1 part by weight of water, at mean temperature. Act of solution at first rapid, then slow, until attainment of point of saturation. Solubility of different salts irrelative to their atomic weights, and variable under different conditions. General increase of solubility with temperature; in same ratio, as with K_2SO_4, $MgSO_4$, KCl, $BaCl_2$; or in more rapid ratio, as $KClO_3$, KNO_3, $Ba(NO_3)_2$. Solubility of common salt scarcely affected by temperature; of hydrate, citrate and butyrate of calcium decreased: and of sulphate of sodium increased up to $33°$, then decreased.

Mutual decomposition of mixed salts in solution. Greater solubility of two salts together in a litre of water, than of the same salts separately in two half-litres.

Differences between well marked cases of solution and chemical combination. Solution effected in indefinite proportions, between more or less allied bodies, which retain more or less of their original properties. Mere solution of anhydrous and hydrated salts, as KNO_3 and $NaSO_4.10H_2O$, alike attended by production of cold. Interference in some cases of initial heat due to act of hydration, as with Na_2SO_4.

Solubility of all gases in water to greater or less extent. Determinate coefficient of solubility of every gas in water and other liquids, under fixed conditions. Solution, for instance, in 100 volumes of water, of 100 volumes CO_2, 16 volumes H_4C_2, and 2 volumes H_2; and in 100 volumes of alcohol, of 288 volumes H_4C_2, at mean temperature and pressure. Increase of temperature attended with decrease of solubility according to no known law. Effect of prolonged boiling to drive off less soluble gases completely. With more soluble gases, except ammonia, to produce distillates of constant composition and boiling point, through establishment of constant ratio between tensions of the gas and aqueous vapour. Evolution of less soluble gases during freezing.

Henry's law of pressure. Equal volumetric solubility of condensed gas as of gas under ordinary pressure. Evolution of gas by removal of pressure. Dalton's more general law. In any mixture of gases, the amount of each gas dissolved dependent on the pressure exerted by that particular gas, *i.e.* on its proportion in the mixture. Hence solution of atmospheric air in water according to product of solubility of each constituent into its proportion; or rather more than $\frac{1}{3}$ oxygen and less than $\frac{2}{3}$ nitrogen.

(19.) PEROXIDE OF HYDROGEN.

Symbol, H_2O_2, or $(HO)_2$. Its production by reaction of carbonic or fluosilicic acid on hydrated peroxide of barium, followed by filtration and evaporation in vacuo. Or, together with some chloride of barium, by action of hydrochloric acid on hydrated peroxide of barium:

$$2HCl + BaO_2.H_2O = BaCl_2 + H_2O_2 + H_2O$$

Further use of sulphuric acid to transform resulting chloride of barium into hydrochloric acid, to be saturated with fresh peroxide of barium, and so on.

Production of peroxide of hydrogen during electrolysis of acidulated water, &c., and during many slow oxidations.

Peroxide of hydrogen a syrupy liquid, of specific gravity 1·45, less volatile than water, and as yet unsolidified. A corrosive, neutral, bleaching and very unstable compound, scarcely known except in form of aqueous solution. The solution more stable, but decomposible below 100°:

$$H_2O_2 = H_2O + O$$

Peroxide of hydrogen recognised by converting chromic acid into peculiar blue compound, soluble in ether.

Its oxidising action upon various substances, including lead-sulphide, iodide of potassium, and certain metallic protoxides. Its precipitation from baryta-water, of hydrated peroxide of barium:

$$BaO.H_2O + H_2O_2 = BaO_2.H_2O + H_2O$$

Its oxidising action upon indigo, &c., facilitated by presence of ferrous sulphate.

Its unlimited decomposition by charcoal, platinum, silver, &c.

Its special reducing action upon iodine, oxide of silver, peroxide of manganese, permanganate, ferrocyanide, and red chromate of potassium, &c.:

$$MnO.O \quad + \quad H_2O.O \quad = \quad MnO \quad + \quad H_2O \quad + \quad OO$$

Account of Brodie's views and experiments.

Relations of water H.HO, and peroxide of hydrogen $(HO)_2$, to hydrochloric acid HCl, and chlorine Cl_2, respectively. Frequent exchange of Cl for HO in mutual conversions of chlorides and hydrylates:

$$K.HO \quad + \quad ClH_3C \quad = \quad KCl \quad + \quad HO.H_3C \quad \text{or} \quad H_4CO$$

(20.) Monad Water-derivatives.

Chlorous derivatives, illustrated by hypochlorous acid HClO, oxide ClClO, and salts MClO. Mutually convertible, unstable, bleaching compounds. Existence of corresponding compounds of bromine and iodine.

Basylous derivatives. The soluble hydrates, LiHO, NaHO, KHO, &c., strongly alkaline compounds, producible by action of respective metals on water, or by double decompositions of their carbonates, sulphates, &c., with hydrates of calcium and barium:

$$K_2CO_3 \quad + \quad Ca(HO)_2 \quad = \quad CaCO_3 \quad + \quad 2KHO$$

Their fusibility at a red heat, without decomposition.

Formation of corresponding oxides, Na_2O, K_2O, &c., by further action of metals on hydrates at higher temperature. Reaction of oxides with water to form hydrates:

$$H_2O \quad + \quad K_2O \quad = \quad \overbrace{KHO \quad + \quad KHO}$$

Insoluble heavy oxides, such as Ag_2O, made by precipitating salts with soluble hydrates:

$$2AgNO_3 \quad + \quad 2KHO \quad = \quad 2KNO_3 \quad + \quad H_2O \quad + \quad Ag_2O$$

Thallous hydrate $TlHO$, decomposed at a red heat. Existence of thallous, aurous, cuprous, and mercurous oxides, Tl_2O, Au_2O, Cu_2O, and Hg_2O.

Derivatives of peroxide of hydrogen, illustrated by $HClO_2$(?), Na_2O_2, Ag_2O_2, &c.

(21.) SULPHUR.

Its occurrence in free state as native sulphur, and in combination with various metals, forming pyrites, blendes, glances, &c. Sulphides of silver, mercury, copper, lead, zinc, and antimony, the chief sources of the several metals. Occurrence of sulphur in oxidised state as sulphates of barium, calcium, magnesium, sodium, &c. Also of unoxidised sulphur in animal and vegetable tissues, &c., particularly albumin.

Native sulphur the chief commercial source of the element. Crude sulphur melted out, or more often distilled off in earthen, and then re-distilled from iron retorts; condensed in the form of flowers, roll, or lump. Some amount of sulphur produced from copper and iron pyrites, by their imperfect combustion in heaps, or roasting in furnaces. Also from refuse oxide of iron-material used in gas purification.

Properties of sulphur. Its yellow colour, insolubility in water, non-conductivity of heat and electricity, and capability of becoming negatively electric by friction.

Effects of heat on ordinary sulphur. Its melting-point under 120°. Remarkable viscid point about 220°. Boiling point 440°. Normal and abnormal vapour-densities of sulphur. Density at 1000°, 32.

Allotropic states of sulphur. Electro-negative or soluble, and electro-positive or insoluble varieties. Disulphide of carbon, and turpentine, the characteristic solvents of sulphur.

Principal electro-negative varieties. Octahedral sulphur, $S\alpha$, the ultimate and most stable form. System the right prismatic. Crystals found native, and deposited from solvents at low temperatures. Specific gravity 2·05. Melting-point 114·5°. Pris-

matic sulphur, $S\beta$. System oblique prismatic. Crystals obtained by fusion, and deposited from hot solvents, as turpentine. Specific gravity 1·98. Melting point 120°. Mutual conversions of octahedral and prismatic sulphur. Their relation to roll and sublimed sulphur. Amorphous soluble sulphur, or milk of sulphur. Greenish white precipitate, thrown down on acidifying alkaline persulphides.

Principal electro-positive, or insoluble varieties. Amorphous insoluble sulphur, thrown down as a bright yellow precipitate by action of water on chloride of sulphur; or of acids on hyposulphite of sodium, from decomposition of hyposulphurous acid:

$$2H_4SO_2 \quad = \quad H_2SO_3 \quad + \quad H_2O \quad + \quad S$$

Its easy oxidisability by nitric acid; and conversion into octahedral sulphur by heat, or digestion with alkaline solutions. Vitreous or plastic sulphur, $S\gamma$, produced in soft, brownish, transparent threads, by suddenly cooling sulphur heated to beyond its viscid point. Its specific gravity 1·95. Its more or less complete conversion, spontaneous or otherwise, into octahedral sulphur, with disengagement of heat. Buff sulphur of various kinds, left by extracting flowers of sulphur, reconverted plastic sulphur, &c., with disulphide of carbon and alcohol. Specific gravity 1·95.

Direct combinations of sulphur with chlorine, and oxygen. Its combustion in air or oxygen to form sulphurous anhydride SO_2. Combustions of hydrogen, phosphorus, carbon, and different metals in sulphur-vapour. Sulphuration of metals in presence of moisture, or sulphur-rusting. Action of strong nitric and sulphuric acids on sulphur, to oxidise and dissolve it. Action of caustic alkalis on sulphur to dissolve it, by reaction similar to that with chlorine:

$$\begin{array}{lclclcl} KHO & + & Cl_2 & = & HClO & + & KCl \\ 2KHO & + & S_2 & = & KHSO_2 & + & KHS \end{array}$$

Solution of additional sulphur in product.

Analogous properties of oxygen gas and sulphur vapour.

Analogy of oxidised and sulphuretted bodies, in constitution and mode of formation, illustrated by CS_2, C_2H_6S, Cl_3PS, KCNS, &c. Existence of sulph-anhydrides, acids, and salts, corresponding to oxi-compounds:

$$2KHS + CS_2 = K_2CS_3 + H_2S$$

Interchangeability of oxygen and sulphur by double decomposition. Equivalency of one atom of sulphur with two atoms of hydrogen or chlorine, shown by chloride and sulphide of ethylphosphine, &c., Et_3PCl_2 and Et_3PS.

(22.) Sulphuretted Hydrogen Gas,

Or sulphydric acid, H_2S; the sulphur analogue of water or steam. Its natural occurrence in volcanic emanations and mineral waters. Also as a result of putrefaction. Its production, like that of water, by direct union of its constituent elements.

Its usual preparation by treating sulphide of iron with dilute sulphuric acid, in various forms of apparatus:

$$H_2SO_4 + Fe''S = Fe''SO_4 + H_2S$$

Or, when required free from hydrogen, by boiling sulphide of antimony with strong hydrochloric acid:

$$6HCl + \overset{'''}{Sb_2}S_3 = 2\overset{'''}{Sb}Cl_3 + 3H_2S$$

Its condensation into the liquid state by cold or pressure, and into the solid state by intense cold. Properties of the gas. Its specific gravity $\frac{2+32}{2} = 17$. Its peculiarly offensive smell and toxic qualities. Solubility of $3\frac{1}{4}$ volumes of the gas in 1 volume of water at 15°, to form a colourless slightly acid liquid, possessing taste and smell of the gas. Consequent collection of the gas by displacement, or over mercury. Its absorbability by charcoal. Its combustion in air or oxygen, to form sulphurous acid H_2SO_3, or $H_2O.SO_2$. Its decomposition by oxygenants, including atmospheric air, with liberation of sulphur. Its decomposition

by metals, with liberation of hydrogen. Its reactions with metallic oxides, chlorides, &c., to form sulphides and sulphydrates:

$$KHO + H_2S = KHS + H_2O$$
$$CuCl_2 + H_2S = CuS + 2HCl$$

Analytical classification of the common metals according to behaviour of their compounds with sulphydric acid and salts. Class I. precipitated from acid solutions by sulphuretted hydrogen. Class II. precipitated from neutral solutions by alkaline sulphides. Class III. precipitated by neither reagent.

I.	II.	III.
Tin	Nickel	Barium
Arsenic	Cobalt	Strontium
Antimony	Manganese	Calcium
Bismuth	Iron	Magnesium
Mercury	Chromium	Potassium
Lead	Aluminum	Sodium
Silver	Zinc	
Copper		
Cadmium		

Persulphide of hydrogen, H_2S_2 (?); made by adding persulphide of calcium or potassium to excess of dilute hydrochloric acid. A heavy, yellowish, unstable oil. Its resemblance to peroxide of hydrogen, in possession of both oxidising and reducing properties, and liability to catalytic decomposition.

(23.) Monad Sulphydric Derivatives.

Persulphide of chlorine, Cl_2S_2; made by passing chlorine gas through melted sulphur and distilling. A heavy, orange-brown, mobile liquid, decomposed by agitation with water into electro-positive sulphur and hydrochloric acid, &c. Its use as a solvent of sulphur in the vulcanising process.

Protosulphide of chlorine, Cl_2S; made by passing chlorine gas into the persulphide. A deep red, mobile liquid, decomposible by admixture with water, and partially, with evo-

lution of chlorine, by ebullition or exposure to light. Tetrachloride of sulphur Cl_4S, not isolable, but known in combination.

The monosulphides of alkali-metal, as K_2S, Na_2S, ill defined colourless compounds, formed in solution by half saturating respective hydrates with sulphuretted hydrogen (?):

$$2KHO + H_2S = 2H_2O + K_2S$$

Pyrophoric monosulphides (?) made by igniting sulphates with lamp-black. The intermediate di-, tri-, and tetra-sulphides, products of definite reactions, and similar in their properties to the pentasulphides, K_2S_5, Na_2S_5, &c.

The pentasulphides, well defined compounds, made by fusing other sulphides, hydrates, &c., with excess of sulphur. Their solubility in water to form deep orange liquids, also producible by boiling sulphide or hydrate solutions with excess of sulphur. Ultimate conversion, by exposure to air, of yellow solutions of different persulphides into colourless solutions of hyposulphites:

$$K_2S_5 + H_2O + O_3 = K_2S_2O_3.H_2O + S_3$$

Sulphydrates of alkali-metal, as KHS, NaHS, well defined, crystallisable compounds, made by saturating solutions of caustic alkali with sulphuretted hydrogen and evaporating down. Their undecomposibility at a red heat, out of contact with air. Behaviour of sulphydrate solutions with nitro-prussides, to yield purple compounds. Their precipitation of heavy metal-salts in deficit, attended with evolution of sulphuretted hydrogen:

$$ZnCl_2 + 2KHS = 2KCl + ZnS + H_2S$$

Solutions of sulphydrates at first colourless, but becoming yellow by oxidation:

$$2KHS + O = K_2S_2 + H_2O$$

Their similar reaction when warmed with sulphur:

$$2KHS + S = K_2S_2 + H_2S$$

Decomposition of alkaline sulphydrates and sulphides by the weakest acids, including even carbonic acid:

$$H_2CO_3 + KHS = KHCO_3 + H_2S$$

Insoluble monosulphides of silver Ag_2S, and cuprosum Cu_2S, found native; and, together with those of mercurosum, thallium, and gold (?) produced as black or brown precipitates by action of sulphuretted hydrogen on solutions of respective metals:

$$2AgNO_3 \quad + \quad H_2S \quad = \quad 2HNO_3 \quad + \quad Ag_2S;$$

or, except that of gold, by direct combinations of metals with sulphur.

Crystalline auro-sulphides, as of sodium $AuNaS.4H_2O$, made by fusing crude gold sulphide with sodium sulphide, digesting in water, and evaporating resultant solution.

(24.) Diad Oxides and Sulphides.

Divisibility of diad metals into a basylous or alkaline earth-, and a more reguline sub-group. Alkaline earth-metals, calcium, strontium, and barium, the diad representatives of potassium and its congeners. The more reguline metals, glucinum (?), magnesium, zinc, cadmium, and mercury, the representatives of sodium and its congeners. Symbols and atomic weights:

G	Glucinum	9			
Mg	Magnesium	24	Ca	Calcium	40
Zn	Zinc	65	Sr	Strontium	87·5
Cd	Cadmium	112	Ba	Barium	137
Hg	Mercury	200			

Special property of mercury to form sub-compounds in addition, as Hg_2O, and $HgCl$ or Hg_2Cl_2, analogous to those of monadic silver.

Hydrates of alkaline earth-metals, CaH_2O_2, SrH_2O_2, and BaH_2O_2, or $Ca(HO)_2$, $Sr(HO)_2$, and $Ba(HO)_2$, well defined compounds, soluble in water, forming caustic liquids corresponding to dilute solution of potash KHO. Their production by action of water on the respective oxides, with great discharge of heat:

$$CaO \quad + \quad H_2O \quad = \quad CaH_2O_2$$

Complete decomposition of calcium-, partial decomposition of strontium-, and indecomposibility of barium-hydrate by ignition.

Oxides of alkaline earth-metals, BaO, SrO, and CaO, made by igniting respective nitrates, and in the case of lime, its hydrate and carbonate also :

$$CaCO_3 \quad = \quad CaO \quad + \quad CO_2$$

Their reactions with water to form above soluble hydrates.

Hydrates of more reguline metals, insoluble, often ill defined compounds, easily rendered anhydrous by heat. Their oxides producible like those of alkaline earth-metals, and by precipitation of respective soluble salts with caustic alkali or alkaline earth, and desiccation :

$$MgCl_2 \quad + \quad Ba(HO)_2 \quad = \quad BaCl_2 \quad + \quad \overbrace{MgO \quad + \quad H_2O}$$

Sulphydrates of alkaline earth-metals, as CaH_2S_2, produced in solution by action of sulphuretted hydrogen on respective hydrates. Their behaviour similar to that of alkali-metal sulphydrates. Sulphides of same metals, as CaS, insoluble compounds gradually decomposed by water, made by igniting respective sulphates with charcoal :

$$CaSO_4 \quad + \quad C_4 \quad = \quad CaS \quad + \quad 4CO$$

Sulphydrates of more reguline metals unknown. Their sulphides made by precipitating salts of the several metals with sulphydric acid or alkaline sulphydrate, and in other ways :

$$CdCl_2 \quad + \quad KHS \quad = \quad KCl \quad + \quad HCl \quad + \quad CdS$$

Sulphides of mercury, cadmium, and zinc, found native in crystalline state, as cinnabar, greenockite, and zinc-blende.

Halogen compounds, as Cl_2Mg, Cl_2Ba, comparable in constitution with hypochlorous oxide Cl_2O, and through it with water H_2O.

Fluoride of calcium F_2Ca, an insoluble, fusible, crystalline compound, found native in abundance. All the chlorides soluble, made by dissolving the several oxides, sulphides, or carbonates in hydrochloric acid and evaporating. Moist chlorides of mag-

nesium and zinc (?) decomposible by heat, with evolution of hydrochloric acid:

$$Cl_2Mg + H_2O = 2HCl + MgO$$

Mercuric chloride usually made by sublimation of mercuric sulphate with chloride of sodium. All the chlorides more or less fusible, and those of the reguline metals volatile in proportion to their atomic weights. Vapour-density of mercuric chloride, Cl_2Hg, $\frac{71+200}{2} = 135\cdot5$. Atomic heat of several chlorides $18\cdot6 = 6\cdot2 \times 3$.

The inferior diad oxides, sulphides, chlorides, &c., formed by metals of higher equivalency, as lead, tin, manganese, iron copper, &c., similar in constitution, and more or less in behaviour, to those of zinc.

(25.) Sulphur Oxacids and Salts.

Comparison of monhydric chlorine- and dihydric sulphur-acids:

HCl	Hydrochloric	H_2S	Sulphydric
$HClO$	Hypochlorous	H_2SO	Wanting
$HClO_2$	Chlorous	H_2SO_2	Hyposulphurous
$HClO_3$	Chloric	H_2SO_3	Sulphurous
$HClO_4$	Perchloric	H_2SO_4	Sulphuric

Dibasicity of sulphur acids shown by formation of both acid and neutral salts, as $KHSO_4$, K_2SO_4, $Ca''SO_4$, &c. Existence of sulphurous and sulphuric anhydrides, SO_2 and SO_3 respectively. Convenient representation of higher acids as compounds of water with anhydride, and as di-hydrylates:

$$H_2SO_3 = H_2O.SO_2 = (HO)_2SO$$
$$H_2SO_4 = H_2O.SO_3 = (HO)_2SO_2$$

Mutual convertibility of sulphydric, sulphurous, and sulphuric acids, by suitable processes of oxidation and deoxidation.

Instability of hyposulphurous acid, and doubtful constitution of hyposulphites or thiosulphates:

$$2NaHSO_2 = Na_2S(O_3S) + H_2O$$

Existence of polythionic series of acids and salts.

SULPHUROUS COMPOUNDS.

Sulphurous anhydride, SO_2; a gas made by burning sulphur in dry air or oxygen. Also by heating sulphur with some metallic oxide, particularly peroxide of manganese:

$$MnO_2 + S_2 = MnS + SO_2$$

Also by reducing sulphuric acid with certain metals, as copper, mercury, silver, &c., or with charcoal or sulphur:

$$Hg'' + \overbrace{H_2SO_4 + H_2O.SO_3} = Hg''SO_4 + 2H_2O + SO_2$$

Specific gravity of gas, $\frac{32 + 16 \times 2}{2} = 32$. Its easy condensation into liquid state by pressure of three atmospheres, or by freezing mixture of salt and ice. Solidification of liquid by its own evaporation in vacuo, or by cold of ether-carbanhydride bath.

Irrespirability of the gas, its smell of burning sulphur, and want of action on dry litmus paper. Its incombustibility, and incapability of supporting combustion, save of phosphorus, sodium, &c., which unite with both its constituents. Its direct combination with the brown peroxide, to form white sulphate of lead:

$$PbO_2 + SO_2 = PbSO_4$$

Sulphurous acid, H_2SO_3 or $H_2O.SO_2$; produced, in state of solution, by saturating water with the anhydride, obtained by burning sulphur or reducing sulphuric acid. In manufactories, the crude gas passed over a coke scrubber; in laboratories, the washed gas passed into distilled water. Solution of 43·5 volumes of sulphurous anhydride in 1 volume of water at 15°. Specific gravity of resulting liquid 1·04. Its odour of burning sulphur, and acidulous property of reddening litmus, effervescing with carbonates, and dissolving many metals. Existence of definite hydrates of sulphurous acid, in solid state, at 0°.

Gradual conversion of aqueous sulphurous into sulphuric

acid by exposure to air. Its frequent employment as a reducing or deoxidising agent. Its reduction of chromates, permanganates, &c. Its reduction of iodic acid with liberation of iodine, so as to form iodide of starch:

$$5H_2SO_3 \quad + \quad 2HIO_3 \quad = \quad 5H_2SO_4 \quad + \quad H_2O \quad + \quad I_2$$

Its further reduction of free chlorine, iodine, &c., so as to bleach iodide of starch:

$$H_2SO_3 \quad + \quad H_2O \quad + \quad I_2 \quad = \quad H_2SO_4 \quad + \quad 2HI$$

Its easy reducibility to the state of sulphuretted hydrogen, by means of nascent hydrogen, stannous chloride, &c., contrasted with difficult reducibility of sulphuric acid. Usual greater permanence of tetra- than of tri-oxygen acids.

Temporary bleaching action of sulphurous acid. Restoration of colour by addition of stronger acid, or neutralisation with alkali. Antiseptic use of sulphur fumes.

Sulphites, M_2SO_3. The soluble salts made by transmitting sulphurous gas through water in which hydrates or carbonates are dissolved or suspended. The acid and neutral sulphites of alkali-metal, and acid sulphites of alkaline earth-metal and magnesium alone soluble. The insoluble sulphites procurable by precipitation. Analogy of the sulphites to carbonates. Their oxidation into sulphates. Their sulphuration into hyposulphites. Their action as antichlores.

Sulphurous chloride, Cl_2SO; made by acting on a neutral sulphite with oxichloride of phosphorus, and in other ways. Sulphurous acid the corresponding hydrate $(HO)_2SO$; thionamide the corresponding amide $(H_2N)_2SO$; and thionamic acid the corresponding hydrate-amide $HO(H_2N)SO$.

SULPHURIC COMPOUNDS.

Marked distinction between acid and anhydride at ordinary temperatures. Existence of moist anhydride at boiling point of acid.

Sulphuric anhydride, SO_3; obtainable by passing mixed oxygen and sulphurous anhydride over heated spongy platinum, oxide of copper, &c.; or preferably by heating oil of vitriol with phosphoric anhydride:

$$H_2SO_4 + P_2O_5 = 2HPO_3 + SO_3{}^*$$

Also by heating Nordhausen oil of vitriol, anhydrosulphate of sodium, &c.:

$$Na_2S_2O_7 = Na_2SO_4 + SO_3$$

A white, fibrous, crystalline, readily fusible and volatile solid. Its violent combination with water and bases. Its decomposition at a red heat:

$$SO_3 = SO_2 + O$$

Fuming sulphuric acid, $H_2S_2O_7$; made at Nordhausen in Prussia, by distilling roughly dried sulphate of iron in earthen retorts. Brown, oily, fuming liquid, of specific gravity 1·9, and nearly uniform composition. Its solidification at 0°, and evolution of anhydride at a gentle heat:

$$H_2S_2O_7 = H_2SO_4 + SO_3$$

Its correspondence to a definite class of salts, known as stylo- or anhydro-sulphates. Its use for dissolving indigo.

Sulphuric acid, H_2SO_4; a product of various reactions. English oil of vitriol made by oxidising moist sulphurous anhydride with air, under influence of certain oxides of nitrogen. Reduction of nitric acid HNO_3, to state of nitric peroxide NO_2, and finally of nitric oxide NO. Alternate oxidation of nitric oxide into peroxide by action of air, and reduction of the peroxide by moist sulphurous anhydride:

$$SO_2 + H_2O + NO_2 = H_2SO_4 + NO$$

In actual manufacture, sulphur burnt on iron plate, or pyrites or gas-refuse burnt in special furnace. Iron pot, containing soda-nitre and sulphuric acid, exposed to heat of burning sulphur, &c.

* Or $H_2O.SO_3 + P_2O_5 = H_2O.P_2O_5 + SO_3$

Mixed sulphurous and nitric vapours conveyed into large leaden chamber, supplied with jets of steam. Dilute sulphuric acid formed on floor of chamber, and drawn off into leaden evaporating pans. Uncondensed gases conveyed into subsidiary chambers, and through coke scrubbers, &c. Final escape of nitrogen of air only (?). Gay-Lussac's process for absorbing nitrous fumes by strong sulphuric acid, and re-using them.

Specific gravity of commercial chamber acid 1·60 and upwards. Its further concentration in leaden pans to 1·72 and upwards. Product known as brown acid. Complete concentration of acid in retorts of glass or platinum, with production of colourless oil of vitriol, and evolution of sulphurous anhydride and carbonous oxide gases, from destruction of organic matter. Purification of acid by distillation, &c.

Normal sulphuric acid H_2SO_4, an oily, colourless, inodorous liquid, of specific gravity 1·842, boiling at 327°, and freezing at −35°. Presence of about 1·25 per cent. excess of water in ordinary acid (De Marignac). Hygroscopic nature of oil of vitriol, and its use as a desiccating agent. Its abstraction of water from various organic compounds, with or without charring.

Combination of sulphuric acid and water, with evolution of heat and contraction of volume. Glacial acid or prot-hydrate, $H_2SO_4.H_2O$. Its specific gravity 1·78. Its property of freezing at +9°, into mass of six-sided prisms, and boiling at 205°, with decomposition. Its production by admixture of acid and water, or by heating weaker acid to 205°.

Deut-hydrate, $H_2SO_4.2H_2O$. Product of mixture of acid and water with maximum of condensation, amounting to nearly 8 per cent. Specific gravity 1·62. Boiling point 192°, with evolution of water only up to 205°. Formation of other hydrates, shown by evolution of heat on admixture of above hydrates with more and more water. Great absorption of heat by dissolving snow in above hydrates. Reactions of strong or dilute acid contrasted with those of anhydride.

Action of sulphuric acid on metals, their oxides and salts, to form sulphates, by an exchange of hydrogen for metal.

Action of strong acid on metals, to evolve sulphurous anhydride:

$$2H_2SO_4 + Hg = HgSO_4 + 2H_2O + SO_2$$

Action of weak acid on more basylous metals, to evolve hydrogen:

$$H_2SO_4 + Zn = ZnSO_4 + H_2$$

Action of acid on oxides or sulphides, to eliminate water or sulphydric acid:

$$H_2SO_4 + FeS = FeSO_4 + H_2S$$

Action on peroxides, to eliminate water and oxygen:

$$H_2SO_4 + MnO_2 = MnSO_4 + H_2O + O$$

Action on salts, to liberate acids:

$$H_2SO_4 + NaCl = NaHSO_4 + HCl$$

Important uses of sulphuric acid as a manufacturing agent, in production of tartaric, acetic, nitric, hydrochloric and other acids, of chlorine and bleaching compounds, of carbonate of sodium, of superphosphate of lime and phosphorus, of sulphate of ammonia and ammoniacal salts, of alum and numerous sulphates, of calomel and corrosive sublimate; and for dissolving silver alloy, dissolving indigo, &c. &c.

Sulphates, M_2SO_4. Very abundant salts, usually obtained as above by acting on the different metals, their hydrates, oxides, and salts, with sulphuric acid. A few of them made by double decomposition with other sulphates, or by oxidising native sulphides, as of iron, zinc, and copper.

Of monad sulphates, those of potassium and sodium, K_2SO_4 and Na_2SO_4, best known, produced in several manufacturing operations, and occasionally found native. Neutral soluble salts unaffected by ignition. The acid or hydrogen sulphates, $KHSO_4$ and $NaHSO_4$, made with excess of acid, and converted into neutral sulphates by ignition. Silver sulphate Ag_2SO_4, a sparingly soluble neutral salt obtainable by precipitation, or by action of sulphuric acid on metallic silver; and reducible again to metallic silver by strong ignition.

Of diad sulphates, those of lead, barium, strontium, calcium, and magnesium found native; $PbSO_4$ and $BaSO_4$ insoluble; $SrSO_4$ almost insoluble; $CaSO_4$ sparingly soluble; $MgSO_4$ and the heavy metal sulphates freely soluble, except that of mercury $HgSO_4$, which is decomposed by water. The heavy metal sulphates possessed of acid reaction, and except those of lead, zinc (?), and manganese (?), decomposed by ignition.

Sulphates of aluminum and iron $\overset{'''}{Al}_2(SO_4)_3$ and $\overset{'''}{Fe}_2(SO_4)_3$, normal triad salts, occasionally found native. Soluble, strongly acid compounds, decomposible on ignition.

Occurrence of many crystalline sulphates as hydrated salts. Replacement in some cases of constitutional water by diad metallic oxide to form basic salts, as $CuSO_4.2CuO.3H_2O$, derived from $CuSO_4.5H_2O$. Existence of basic triad sulphates. Basic salts for the most part insoluble in, or decomposible by, water.

Existence of double sulphates formed on the type of two atoms of sulphuric acid, $H_4S_2O_8$. Principal varieties exemplified by potassium-ferrous sulphate $K_2FeS_2O_8.6H_2O$, and alum $KAlS_2O_8.12H_2O$. Soluble salts, decomposible into their constituent sulphates by excess of water, or by diffusion.

All soluble sulphates, including sulphate of hydrogen, recognised by giving with barium-solutions a white precipitate of barium-sulphate, insoluble in nitric (?) and hydrochloric acids. All sulphates, including above barium-sulphate, converted by ignition with charcoal and carbonate of sodium into mass containing soluble sulphide, recognisable by producing black stain on silver coin, &c.

Representation of sulphuric chloride, acid, and amide, on double hydrochloric acid, water, and ammonia types respectively:

$$(SO_2)''Cl_2 \qquad \left.\begin{matrix}(SO_2)''\\ H_2\end{matrix}\right\}O_2 \qquad \left.\begin{matrix}(SO_2)''\\ H_2\\ H_2\end{matrix}\right\}N_2$$

Sulphuric chloride, Cl_2SO_2; made by direct combination of chlorine and sulphurous anhydride under exposure to sunlight; and by various reactions. Sulphuric acid the corresponding hydrate $(HO)_2SO_2$, and sulphamide the corresponding amide $(H_2N)_2SO_2$. Intermediate compounds exemplified by $Cl(HO)SO_2$, $Cl(H_2N)SO_2$, and $HO(H_2N)SO_2$.

HYPOSULPHUROUS COMPOUNDS.

The acid practically non-existent, undergoing decomposition, with separation of electro-positive sulphur, almost immediately on being set free:

$$2H_2SO_2 \quad = \quad H_2SO_3 \quad + \quad H_2O \quad + \quad S$$

Constitution of salts doubtful. Representation of sodium-hyposulphite as an analogue of the formiate, or as a hydrated thiosulphate:

$$2NaHSO_2 \quad = \quad Na_2S(O_3S).H_2O$$

The hyposulphites producible by dissolving sodium, zinc, iron, &c., in aqueous sulphurous acid. Process analogous to that yielding formiates:

$$Na_2 \quad + \quad 2H_2SO_3 \quad = \quad NaHSO_3 \quad + \quad NaHSO_2 \quad + \quad H_2O$$

Hyposulphite of sodium, $Na_2S_2O_3.H_2O.4H_2O$; a commercial salt, made by passing sulphurous acid gas through a solution of alkaline sulphide, or preferably by digesting sulphur with a solution of the neutral sulphite:

$$Na_2SO_3 \quad + \quad S \quad + \quad H_2O \quad = \quad Na_2S_2O_3.H_2O$$

Also by boiling sulphur with solution of caustic soda and exposing yellow liquid to the air till colourless; by decomposing crude hyposulphite of calcium, in gas-lime refuse and ball-soda refuse, with carbonate of sodium, &c.

The hyposulphites of alkali-, alkaline earth-metal, and magnesium soluble in water. That of barium only sparingly soluble, and procurable as a crystalline precipitate by double decomposition.

Action of soluble hyposulphites on most heavy metallic oxides and salts, especially at a gentle heat, to form sulphides:

$$HgO + Na_2S_2O_3.H_2O = HgS + Na_2SO_4 + H_2O$$

Similar behaviour of hyposulphite of sodium on chloride of silver that has been altered by light. Its solution of the unaltered chloride, with formation of sweet-tasting double salt; whence its use in photography:

$$AgCl + Na_2S_2O_3.H_2O = NaCl + AgNaS_2O_3.H_2O$$

Crystalline double hyposulphite of gold and sodium $Au'Na_3(S_2O_3.H_2O)_2$, made by mixing gold trichloride with sodium-hyposulphite, in concentrated aqueous solution, and precipitating by alcohol, &c.

Use of hyposulphite of sodium as an antichlore, for neutralising the last traces of chlorine in bleached goods. Its similar decoloration of free iodine. Tetrathionate produced by action of iodine, free chlorine, and chlorine of perchlorides, as of gold, on hyposulphites:

$$Cl_2 + 2(Na_2S_2O_3.H_2O) = 2NaCl + Na_2S_4O_6 + 2H_2O$$

POLYTHIONIC COMPOUNDS.

A series of salts referrible to the following more or less unstable acids:

$H_2S_2O_6$	Dithionic
$H_2S_3O_6$	Trithionic
$H_2S_4O_6$	Tetrathionic
$H_2S_5O_6$	Pentathionic

Manganous dithionate, or hyposulphate, made by action of sulphurous acid gas on peroxide of manganese suspended in cold water:

$$MnO_2 + 2SO_2 = MnS_2O_6$$

Decomposition of dithionates by heat, into sulphate and sulphurous anhydride:

$$MnS_2O_6 = MnSO_4 + SO_2$$

Similar decomposition of the other polythionates with formation of sulphate, sulphurous anhydride, and sulphur. The tetrathionates, salts of some stability and importance, usually made by action of iodine on hyposulphites:

$$I_2 \quad + \quad 2(BaS_2O_3.H_2O) \quad = \quad BaI_2 \quad + \quad BaS_4O_6 \quad + \quad 2H_2O$$

(26.) Selenium and Tellurium.

Selenium very analogous to sulphur; tellurium semi-metallic, like arsenic. Both elements found native, and in form of metallic selenides and tellurides. Occurrence of selenium as a partial substitute for sulphur in various sulphides. Selenium less chlorous, and tellurium far less chlorous than sulphur, shown by their more easy separation from hydrogen and the basylous metals, and in other ways. Existence of selenium and tellurium representatives of sulphydric, sulphurous, and sulphuric acids, &c.:

H_2S	SO_2	H_2SO_4
H_2Se	SeO_2	H_2SeO_4
H_2Te	TeO_2	H_2TeO_4

CHAPTER IV.

(27.) Nitrogen Elements.

Nitrogen—Phosphorus, Arsenic, Antimony—Bismuth.

Their property of combining with hydrogen or its representatives in the ratio of one atom to three. Production of more or less alkaline terhydrides, &c. Bismuth-hydride unknown. Symbols and atomic weights:

N	Nitrogen	14	
P	Phosphorus	31	mean 76
As	Arsenic	75	
Sb	Antimony	122	
Bi	Bismuth	210	

Special characters of nitrogen and bismuth. Antimony intermediate in position between phosphorus and bismuth. Strictly gradational properties of phosphorus, arsenic, and antimony. Gradual development of metallic characters in lower members of the group.

(28.) Nitrogen.

Its abundant occurrence as free nitrogen in the air. Its existence in potash- and soda-nitres to the extent of 14 and 16 per cent.; also in ammonia, guano, coal, and various organic substances. Inertness of nitrogen in free state contrasted with its activity in combination. Varied character of nitrogenous bodies, such as albumin, gelatin, the natural and artificial alkaloids, ammonia, prussic acid, gun-cotton, nitric acid, colouring matters in general, &c. &c.

Separation of nitrogen from the atmosphere by removal of oxygen, moisture, and carbanhydride. Variety of deoxygenants

employed, including phosphorus, whether or not inflamed, ignited copper, moist sulphide of iron, solution of alkaline pyrogallates, &c. Nitrogen also procurable from ammonia by action of chlorine or other oxygenant; and from oxides, acids, and oxisalts of nitrogen by means of ignited iron, or other reducant, &c. Its easy production by decomposition of nitrite of ammonia, or nitrate of ammonia and zinc:

$$NH_3.HNO_2 = 2H_2O + N_2$$
$$Zn + NH_3.HNO_3 = 2H_2O + N_2 + ZnO;$$

also, together with chlorine, by heating mixed nitrate and hydrochlorate of ammonia.

Nitrogen a colourless, tasteless, inodorous, neutral gas, incondensable and almost insoluble. Its specific gravity of 14, somewhat less than that of atmospheric air. Its incapability of burning and supporting ordinary combustion and respiration. Its generally negative characters. Its combination with oxygen, by passage of electric sparks through mixed gases, to form nitric peroxide, &c. Its gradual combination with nascent hydrogen, to produce ammonia. Formation of cyanides, by its transmission over ignited mixture of charcoal and caustic alkali or alkaline earth.

Its indirect replacement of three atoms of hydrogen in certain organic compounds.

(29.) Atmospheric Air.

A mixture of about four volumes of nitrogen and one volume of oxygen, with small proportions of aqueous vapour, carbanhydride, and other gases and vapours.

A colourless, tasteless, inodorous, incondensable gas, about 770 times lighter than water. Its specific gravity 14·47, compared with that of hydrogen as unity. Weight of one litre of air, freed from moisture and carbanhydride, at 760 mm. and 0°, 1·293 grammes. Weight of 100 cubic inches of same air at 60° F., 30·935 grains. (Regnault.)

The atmosphere a supporter of combustion and respiration by virtue of its constituent oxygen. At ordinary temperatures its

action as an oxygenant for the most part slow, but very extensive in results. Rusting of metals in air, by conjoint influence of oxygen, moisture, and carbanhydride. Disintegrating action of atmospheric moisture on rocks, &c.

Exact composition of the atmosphere. Lavoisier's experiment of heating metallic mercury in air so to leave the nitrogen, and then further heating resultant oxide of mercury to obtain the oxygen. Early analyses of air by Scheele, and Priestley, and Cavendish. Modern eudiometric analysis by absorption of oxygen with ball of phosphorus, alkaline pyrogallate, &c., or by explosion of air with hydrogen. In last case, one-third of resulting contraction due to oxygen. Mean result of Regnault's numerous explosion determinations :

	By volume	By weight
Oxygen	20·93	23·13
Nitrogen	79·07	76·87

Analysis of air by weight. Process of Dumas and Boussingault, by drawing air, deprived of moisture and carbanhydride, through weighed and exhausted porcelain tube containing spongy copper at a red heat, and thence into large vacuous flask. Quantity of air experimented on shown by increase of weight in flask and tube jointly. Proportion of oxygen shown by the increase of weight in tube, after re-exhaustion by air-pump. Mean result :

	By volume	By weight
Oxygen	20·8	23·0
Nitrogen	79·2	77·0

Existence of moisture in air, shown by deposition of dew or hoar-frost on vessels containing ice or freezing mixture. Also by moistening of various deliquescent substances, such as chloride of calcium, caustic potash, oil of vitriol, &c. Its presence chiefly due to evaporation, partly to combustion and respiration. Its proportion very variable; on an average about 1·4 or 1·5 per cent. Its estimation by drawing air over pumice soaked in oil of vitriol, &c.; also by torsion-, wet-tube-, and dew-point hygrometers.

Existence of carbanhydride in air, shown by formation of

opaque films of carbonate on exposed lime-water, basic acetate of lead solution, &c. Its origin from combustion, respiration, and volcanic discharges, &c. Its average proportion in open air 0·04 per cent., and range from 0·03 to 0·06 per cent. Its maximum in crowded and artificially illuminated rooms 0·33 per cent (?). Its quantity estimated by drawing dry air over solid moist caustic potash, &c. Pettenkofer's volumetric process performed by agitating air with lime-water, and then estimating excess of caustic lime with standard solution of oxalic acid. Average composition of the atmosphere by volume:

Nitrogen	77·95
Oxygen	20·61
Moisture	1·40
Carbanhydride	0·04
	100·00

Minute atmospheric constituents, including ammonia, found in rain-water to extent of one grain in 14 gallons of country rain (Lawes and Gilbert), nitric acid, free hydrogen, marsh-gas, sulphurous acid, organic matter, &c.

Despite its practical invariability of composition, the air a mechanical mixture of gases,—not a chemical combination. Proofs afforded by the separability of its constituents by diffusion, solution, and feeble chemical action. By its refrangibility, density, &c. being the exact means of those of its constituents. By its artificial production on mixing oxygen and nitrogen in right proportions. By the ratio of the two gases to each other being neither atomic nor absolutely invariable. Observed variation in proportion of oxygen from 20·8 to 21·0 per cent.

Invariable composition of the atmosphere at different times consequent on its immense mass. Also on balance of animal and vegetable functions. Evolution of oxygen and absorption of carbanhydride by growing plants. Evolution of carbanhydride and absorption of oxygen by breathing animals.

Invariable composition of the atmosphere at different places, brought about by winds or currents, and gaseous diffusion.

(30.) Ammonia.

Symbol, H_3N or NH_3. Extensive natural distribution of minute quantities of ammonia, as in rain-, river-, spring-, and sea-water, clay, marl, ochre, and some varieties of rock-salt, &c. Its occurrence in juices of plants, and most animal fluids, especially the urine. Also in guano, and as native ammonia-alum, triple phosphate, &c.

Inconsiderable formation of ammonia by union of its constituent elements under various circumstances, and more abundantly by hydrogenation of nitric acid and different oxides of nitrogen; also by hydration of cyanides, &c.:

$$KCN + 2H_2O = KHCO_2 + H_3N$$

Its occurrence as a result of putrefaction, and of the destructive distillation of animal matter, alone or with soda-lime. Its extensive production by the distillation of coal in gas works. Redistilled gas liquor usually neutralised with sulphuric acid and evaporated down. Resulting sulphate of ammonia sublimed with common salt to form sal-ammoniac, or with chalk to form carbonate of ammonia.

Gaseous ammonia obtained by heating mixture of sal-ammoniac and quicklime:

$$CaO + 2NH_3HCl = CaCl_2 + 2NH_3 + H_2O$$

Gas collected by upward displacement, or over mercury. Absorption of ammonia by water, alcohol, chloride of silver or calcium, &c., and its reliberation by heat. Gaseous ammonia most readily obtained by heating the aqueous solution. Its desiccation by potash or lime. Its absorption by charcoal.

Condensation of ammonia at $-40°$, or under pressure of 7 atmospheres at $15°$, into a liquid, solidifiable in ether-carb-anhydride bath. Liquid ammonia best obtained by heating ammonio-chloride of silver in one limb of sealed Λ tube,—the other being kept cool by ice.

Specific gravity of gaseous ammonia $\frac{3+14}{2} = 8{\cdot}5$. Its pun-

gent smell, and irrespirability, save when considerably diluted. Its alkalinity, shown by its power of neutralising acids and affecting vegetable colours.

Decomposition of 2 volumes of ammonia by electric spark, into 1 volume of nitrogen and 3 volumes of hydrogen,—the original 2 volumes becoming 4. Reaction of 3 volumes of chlorine upon ammonia, to set free 1 volume of nitrogen :

$$H_3N + Cl_3 = 3HCl + N*$$

Feeble combustibility of ammonia in oxygen or air. Its slow oxidation into nitrous acid, or a nitrite, under various circumstances. Reaction of alkali-metals on ammonia to liberate hydrogen.

Solution of ammonia made by passing the gas, as liberated from sal-ammoniac by slaked lime, into cold water, usually contained in series of Wolfe's bottles. Conversion of two volumes of water into three volumes of solution, with considerable evolution of heat. Absorption of 783 volumes of ammonia-gas by 1 volume of water at 15°. Specific gravity of saturated solution 0·850. Its solidification at −40°. Gas evolved from exposed solution at ordinary temperatures, and rapidly when heated, with appearance of ebullition. Complete discharge of gas by continued real ebullition. Great solubility of ammonia in alcohol, ether, &c.

AMMONIA SALTS.

Direct combination of ammonia with acids, to form ammonia-salts. Their alternative representation as ammonium-salts, analogous to those of potassium :

$NH_3.HCl$	$(NH_4)Cl$	KCl
$NH_3.HNO_3$	$(NH_4)NO_3$	KNO_3
$NH_3.H_2SO_4$	$(NH_4)HSO_4$	$KHSO_4$
$2NH_3.H_2SO_4$	$(NH_4)_2SO_4$	K_2SO_4

General isomorphism, and other resemblances, between potassium- and ammonium-salts. Similar electrolytic productions of potassium- and ammonium-amalgams. Action of sodium-

* Or $2H_3N + Cl_6 = 6HCl + N_2$

amalgam on sal-ammoniac solution to set free bulky unstable ammonium-amalgam:

$$NH_4Cl \quad + \quad NaHg \quad = \quad NaCl \quad + \quad NH_4Hg.$$

Ammonium-salts for the most part neutral, colourless, crystallisable, insipid, and odourless compounds, freely soluble in water, and to some extent in spirit of wine. Partial decomposition of solutions of most ammonium-salts during their evaporation, with evolution of ammonia.

Action of heat on ammonium-salts. Volatilisation of some, as hydrochloride. Correspondence of vapour to 4 volumes; owing to its dissociation into 2 volumes of hydrochloric acid and 2 volumes of ammonia? Decomposition of other salts, with separation of acid as phosphate, or reduction of acid as chromate. Intermediate effect of heat on oxisalts to drive off water. Production of amides by abstraction of one atom of water for each atom of ammonia in salt, as in conversion of formiate of ammonia into formiamide:

$$NH_3.H_2CO_2 \quad - \quad H_2O \quad = \quad NH_2.HCO$$

Production of nitriles by abstraction of two atoms of water for each atom of ammonia in salt, as in conversion of same salt into formio-nitrile or prussic acid:

$$NH_3.H_2CO_2 \quad - \quad 2H_2O \quad = \quad NHC$$

Identification of ammonium-salts. Their decomposition by fixed bases, with evolution of free ammonia, recognisable by its reaction, smell, and in various ways:

$$NH_4Cl \quad + \quad KHO \quad = \quad KCl \quad + \quad \overbrace{NH_3 \quad + \quad H_2O}$$

Precipitability of their solutions by tartaric acid, tetrachloride of platinum, phospho-molybdate of sodium, potash iodide of mercury, &c.

Principal salts of ammonium. The sulphate $(NH_4)_2SO_4$, made by neutralising sulphuric acid with distilled gas liquor. The chloride NH_4Cl, made by saturating certain cheap chlorides, as of hydrogen, calcium, and manganese, with distilled gas

liquor, or by subliming sulphate of ammonia with common salt:

$$(NH_4)_2SO_4 \quad + \quad 2NaCl \quad = \quad Na_2SO_4 \quad + \quad 2NH_4Cl$$

The commercial sesquicarbonate made by subliming chloride or sulphate of ammonium with chalk.* A pure but very complex salt, consisting of two atoms of acid-carbonate of ammonium, $2NH_4HCO_3$, and one atom of carbamate, $NH_4(NH_2)CO_2$, or neutral carbonate, minus an atom of water:

$$(NH_4)_2CO_3 \quad - \quad H_2O \quad = \quad NH_4(NH_2)CO_2, \quad \text{or} \quad (NH_3)_2CO_2$$

A pungent smelling salt, converted into acid carbonate by exposure to air, through volatilisation of carbamate.

The hydrate $NH_4.HO$, considered to result from combination of ammonia and water, as in ordinary solution of ammonia. Its behaviour with salts of iron, zinc, uranium, &c. similar to that of caustic potash KHO. Special action of aqueous ammonia on some metallic salts, as those of mercury, to form amides:

$$Cl_2Hg'' \quad + \quad 2NH_3 \quad = \quad Cl(NH_2)Hg'' \quad + \quad NH_4Cl$$

Other ammonium-salts made by neutralising the sesquicarbonate, or aqueous ammonia, with the respective acids.

Direct combination of ammonia with various metallic salts, as with chloride of silver, $AgCl.2NH_3$, of zinc $ZnCl_2.4NH_3$, of calcium $CaCl_2.8NH_3$, &c.

(31.) Ammonia Derivatives.

Possibility of replacing 1, 2, or 3 atoms of hydrogen in ammonia, by halogen, metal, or radical.

Trichloramine, or chloride of nitrogen, Cl_3N; made by action of excess of chlorine on ammonia, or preferably sal-ammoniac, and in other ways:

$$H_3N.HCl \quad + \quad Cl_6 \quad = \quad Cl_3N \quad + \quad 4HCl$$

A thin, heavy, and most violently explosive oil.

$$* \begin{cases} 3(NH_4)_2SO_4 \quad + \quad 3Ca''CO_3 \quad = \quad 3Ca''SO_4 \quad + \quad 3(NH_4)_2CO_3 \\ 3(NH_4)_2CO_3 - 2NH_3 - H_2O \quad = \quad 2NH_4HCO_3.NH_4(NH_2)CO_2 \end{cases}$$

Diniodamine, or iodide of nitrogen, I_2HN; made by digesting powdered iodine in strong solution of ammonia:

$$\overline{H_3N + 2H_3N} + I_4 = I_2HN + 2(H_3N.HI)$$

A soft brownish-black powder, violently explosive when dry.

Potassamine, KH_2N; a grey fusible solid, made by heating potassium in dry ammonia gas:

$$2H_3N + K_2 = 2KH_2N + H_2$$

Its conversion into tripotassamide when strongly heated:

$$3KH_2N = K_3N + 2H_3N;$$

and reaction with water to form caustic potash:

$$KH_2N + H_2O = H_3N + KHO$$

Sodium-compounds, NaH_2N and Na_3N, similar to above in properties and mode of formation. Existence of analogous zinc compounds, $Zn''H_4N_2$ and Zn_3N_2, &c. &c.

Reference of potassium, &c., -chloride, -hydrate, -oxide, and -amides, to hydrochloric acid, water, and ammonia types:

$$KCl \qquad \left.\begin{matrix}K\\H\end{matrix}\right\}O \qquad \left.\begin{matrix}K\\H\\H\end{matrix}\right\}N$$

$$\left.\begin{matrix}K\\K\end{matrix}\right\}O \qquad KKHN$$

$$KKKN$$

Correspondence of radicals, chlorine Cl, and hydroxyl HO, to amidogen H_2N; and of chlorides and hydrates to amides, as HCl and KCl, H.HO and K.HO, to $H.H_2N$ and $K.H_2N$, &c. Existence of simple or complex amides, corresponding to various chlorides and hydrates, illustrated by mercuric, zincic, sulphuric, and phosphoric chlorides, hydrates, amides, chloro-hydrates, chlor-amides, and amid-hydrates:

Cl_2Hg	$Cl(H_2N)Hg$		Cl_2Zn	$(H_2N)_2Zn$
Cl_2SO_2	$Cl(HO)SO_2$	$(HO)_2SO_2$	$HO(H_2N)SO_2$	$(H_2N)_2SO_2$
Cl_3PO	$(HO)_3PO$	$(HO)_2H_2NPO$	$HO(H_2N)_2PO$	$(H_2N)_3PO$

Hydroxylamine, H_3NO; a basic derivative of water by replacement of amidogen for hydrogen $(H_2N)HO$, or of ammonia by replacement of hydroxyl for hydrogen $(HO)H_2N$. A product of the action of nascent hydrogen on nitric acid, intermediate between nitric acid and ammonia:

$$HNO_3 \quad + \quad H_6 \quad = \quad H_3NO \quad + \quad H_2O \quad + \quad H_2O$$

In actual process, nitrate of ethyl substituted for nitric acid, and hydrogen made by action of hydrochloric acid upon tin:

$$EtNO_3 \quad + \quad H_6 \quad = \quad H_3NO \quad + \quad EtHO \quad + \quad H_2O$$

Resulting hydrochlorate of hydroxylamine extracted from evaporated residue by strong alcohol, and purified by crystallisation. Salts of the base well defined and easily crystallisable. The base itself known only in solution, volatile in the vapour of water, and very unstable:

$$3H_3NO \quad = \quad 3H_2O \quad + \quad H_3N \quad + \quad N_2$$

(32.) Oxides and Acids of Nitrogen.

Comparison of oxides of hydrochloric acid, sulphuretted hydrogen, and phosphine:

HCl	H_2S	H_3P
$HClO$	H_2SO	H_3PO
$HClO_2$	H_2SO_2	H_3PO_2
$HClO_3$	H_2SO_3	H_3PO_3
$HClO_4$	H_2SO_4	H_3PO_4

Distinction between ortho-phosphoric acid H_3PO_4, and meta-phosphoric acid HPO_3:

$$H_3PO_4 \quad - \quad H_2O \quad = \quad HPO_3$$

Ordinary nitrous and nitric acids meta-compounds, comparable with meta-phosphoric acid:

Nitrous acid	HNO_2	$(= H_3NO_3 - H_2O)$
Nitric acid	HNO_3	$(= H_3NO_4 - H_2O)$

Apparent existence of a few ortho-nitrites and ortho-nitrates. Mutual conversion of ordinary nitrites and nitrates, by oxidation and reduction respectively. Relationship of nitrous acid HNO_2, nitrogen N_2, and ammonia H_3N, to one another.

Series of nitrogen-oxides, all procurable from, and directly or indirectly convertible into, nitric acid:

	N_2O	Nitrous oxide
NO or	N_2O_2	Nitric oxide
	N_2O_3	Nitrous anhydride
NO_2 or	N_2O_4	Nitroso-nitric anhydride
	N_2O_5	Nitric anhydride

Relation of the anhydrides to their respective acids:

$$N_2O_3 + H_2O = 2HNO_2$$
$$N_2O_4 + H_2O = HNO_3 + HNO_2$$
$$N_2O_5 + H_2O = 2HNO_3$$

Formulation on water-type of both acids and anhydrides, thus:

$$\left.\begin{matrix}H\\H\end{matrix}\right\}O;\quad \left.\begin{matrix}H\\NO\end{matrix}\right\}O,\quad \left.\begin{matrix}NO\\NO\end{matrix}\right\}O,\quad \left.\begin{matrix}NO\\NO_2\end{matrix}\right\}O,\quad \left.\begin{matrix}NO_2\\NO_2\end{matrix}\right\}O,\quad \text{and}\quad \left.\begin{matrix}H\\NO_2\end{matrix}\right\}O.$$

Identity of expressions $\left.\begin{matrix}H\\NO_2\end{matrix}\right\}O$, or $H(NO_2)O$, and $HO.NO_2$, &c.

NITROUS OXIDE.

Symbol, N_2O. Its formation by heating nitrate of ammonia. Abstraction from the salt of twice as many atoms of water as it contains atoms of ammonia, so as to yield the nitrile:

$$NH_3HNO_3 = 2H_2O + N_2O$$

Its production during many reductions of different oxides of nitrogen, as of nitric oxide with moist iron-filings, of dilute nitric acid with zinc, &c.

Nitrous oxide, a heavy gas, of specific gravity $\frac{28+16}{2} = 22$. Its liquefaction by pressure of 32 atmospheres at 0°; and solidification by spontaneous evaporation of the liquid, or by exposure of

it to cold of ether-carbanhydride bath. Reduction of thermometer to lowest observed temperature, namely $-140°$ C., or $-284°$ F., by evaporation in vacuo of solidified nitrous oxide dissolved in disulphide of carbon.

Solubility of 78 volumes of nitrous oxide in 100 volumes of water at 15°. Its yet greater solubility in alcohol. Neutrality of its solutions.

Brilliant combustion of ordinary combustibles in nitrous oxide. Its property of re-inflaming a glowing taper, similar to that of oxygen. Its want of action, however, on alkaline pyrogallates, nitric oxide, &c. The combustible elements, except carbon, not readily inflammable in nitrous oxide, save when strongly heated so as to produce decomposition of the gas.

Decomposition of nitrous oxide at a red heat, or by transmission of electric sparks, into two volumes of nitrogen and one of oxygen. Result of its explosion with an equal volume of hydrogen:

$$N_2O \quad + \quad H_2 \quad = \quad H_2O \quad + \quad N_2$$

Its stimulant and anæsthetic properties, whence its familiar name of laughing gas.

NITRIC OXIDE.

Symbol, NO, or N_2O_2. Its liberation by reduction of diluted nitric acid with metallic copper, mercury, silver, &c., or with acid solution of ferrous salts:

$$Cu''_3 \quad + \quad \overbrace{6HNO_3 \quad + \quad 2HNO_3} \quad = \quad 3Cu''(NO_3)_2 \quad + \quad 4H_2O \quad + \quad 2NO$$

Its occurrence also as a product of the oxidation of ammonia by means of ignited peroxide of manganese, red chromate of potassium, &c.

Unlike nitrous oxide, an incondensable, sparingly soluble gas, but slightly heavier than atmospheric air; not decomposible, if perfectly dry, by the electric spark or a red heat; and not susceptible of explosion with hydrogen. Solubility of 5 volumes

of nitric oxide in 100 volumes of water at 15°. Specific gravity of the gas $\frac{14+16}{2}=15$.

Direct combination of nitric oxide with oxygen at ordinary temperatures, to produce brown fumes dissolving in water to form acid solution. Nitric oxide itself devoid of acid character. Temporary absorption of gas by ferrous solutions, to form compounds such as $2FeSO_4.NO$. Its oxidation by nitric acid; and absorption by oxide of silver, peroxide of manganese, &c., with formation of nitrites.

Its reduction to state of nitrous oxide by sulphurous acid, moist iron-filings, &c. Its further reduction to the state of nitrogen by moist iron-filings and sulphur, and by combustions. Flame of ordinary combustibles extinguished by nitric oxide. Combustion, however, of strongly ignited phosphorus, carbon, and basylous metals, very brilliant. Also of disulphide of carbon, with evolution of intensely actinic light. Production of one volume of nitrogen from two volumes of gas, by ignited carbon, metals, &c. Further reduction of nitric oxide to state of ammonia, by excess of sulphuretted hydrogen at a red heat.

Existence of a sulphur analogue to nitric oxide, N_2S_2, in form of golden yellow crystals.

Direct combination of nitric oxide with chlorine to form nitrous chloride or chloride of azotyl, ClNO, or (NO)Cl. Existence of same compound in aqua-regia, as a product of the action of nitric upon hydrochloric acid. Its occurrence as a deep orange-coloured gas, condensable by cold into a red fuming liquid. Its reaction with water or alkali to form nitrite and chloride of hydrogen or metal:

$$HHO \quad + \quad ClNO \quad = \quad HNO_2 \quad + \quad HCl$$

Formation in oil of vitriol chamber of different crystalline sulphates of azotyl, especially of the anhydro-sulphate $(NO)_2S_2O_7$. Other salts of azotyl known, as the nitrate $(NO)NO_3$, or nitric peroxide, &c.

NITRITE COMPOUNDS.

Nitrites. Products of the oxidation of ammonia, nitric oxide, &c., in presence of bases, and of the reduction of nitric acid or nitrates. Colourless or slightly yellow salts, usually made by condensing nitrous fumes in alkali-solutions and evaporating; or by igniting nitrates, with or without charcoal or metal to abstract oxygen:

$$KNO_3 \quad = \quad KNO_2 \quad + \quad O$$

Nitrites, except those of silver and lead, readily soluble in water, and many of them also in alcohol. Fusibility of most nitrites at a moderate heat, their decomposition at a stronger heat, and deflagration with combustible matter. Reaction of alkali-nitrites with copper solutions to produce a bright green colour; and with silver solutions to throw down a white crystalline precipitate. Nitrites converted into nitrates by exposure of their warm solutions to air. Decomposition of nitrite solutions in general, by prolonged ebullition, and rapid decomposition of that of nitrite of ammonia:

$$NH_3HNO_2 \quad = \quad 2H_2O \quad + \quad N_2$$

Nitrous acid, HNO_2. A very unstable compound, readily breaking up into nitric acid, water, and nitric oxide; but more permanent in presence of much nitric acid:

$$\overbrace{HNO_2 \quad + \quad 2HNO_2} \quad = \quad HNO_3 \quad + \quad H_2O \quad + \quad 2NO$$

Production of nitrous acid by acidifying ice-cold solutions of the nitrites. Its tendency to form nitric acid, whence its reducing action on permanganic and chromic acids, &c. Its action as an oxidising agent to bleach indigo, set free iodine, convert ferrous into ferric salts, &c.

$$2HNO_2 \quad = \quad O \quad + \quad H_2O \quad + \quad 2NO$$

Nitrous acid recognised even in weak solution by its liberation of iodine from iodide of potassium, production of olive-brown

compound with sulphate of iron, &c. Similar results produced by nitric acid only when in concentrated state.

Nitrous anhydride, N_2O_3. Its formation by mixing large excess (4 volumes) of nitric oxide with oxygen (1 volume), and passing mixed gas through freezing mixture; or by deoxidising nitric acid with arsenious oxide, starch, &c., and passing resultant brown vapours through freezing mixture:

$$2HNO_3 \text{ or } H_2O.N_2O_5 + As_2O_3 = H_2O.As_2O_5 + N_2O_3$$

Its occurrence as a very volatile, unstable, bright blue liquid, giving off brown fumes. Its reaction with ice-cold water to form blue solution of nitrous acid, rapidly changing into nitric acid, water, and nitric oxide:

$$H_2O + N_2O_3 = 2HNO_2$$

Its reaction with alkalies to form moderately stable nitrites:

$$K_2O + N_2O_3 = 2KNO_2$$

Its solubility in not too strong nitric acid to form blue mixture of nitric and nitrous acids.

NITRIC PEROXIDE.

Symbol, NO_2; or as nitroso-nitric anhydride, N_2O_4. Its production by admixture of excess of nitric oxide gas (2 volumes) with oxygen (1 volume). Condensation of mixed gas, by cold of ice and salt, into a liquid, and if absolutely dry, into a crystalline compound.

Nitric peroxide best made by distillation of dry nitrate of lead in porcelain retort:

$$Pb(NO_3)_2 = PbO + N_2O_4 + O$$

In complete absence of moisture, product obtained in form of white prismatic crystals, melting at $-9°$. Increase in colour of ordinary liquid product with temperature, from pale yellow to deep orange; in presence of trace of moisture, greenish. Its boiling point 22°. Similar increase in colour of gas or vapour with

temperature, from pale orange to almost black at 40°. Specific gravity of gas $\frac{14+32}{2}=23$. Its behaviour with ignited combustibles similar to that of nitric oxide. Nitric peroxide devoid of acid properties when perfectly dry. Its reaction with alkalies to form nitrate and nitrite of metal:

$$K_2O + N_2O_4 = KNO_3 + KNO_2$$
$$H_2O + N_2O_4 = HNO_3 + HNO_2$$

Its reaction with minute quantity of water to form nitric acid and nitrous acid or anhydride; and with excess of water, to form nitric acid and products of decomposition of nitrous acid, namely, nitric acid, water, and nitric oxide,—liquid becoming successively blue, green, and orange yellow. Solubility of nitric peroxide in strong nitric acid to form orange-yellow liquid, miscalled nitrous acid.

Occasional reducing action of nitric peroxide, as upon permanganates, by reason of nascent nitrous acid acquiring oxygen to become nitric acid. Its chief action that of a powerful oxygenant, with self-reduction into nitric oxide, nitrous oxide, nitrogen, and ammonia, successively.

Nitric peroxide, or nitryl, regarded as a radical analogous to chlorine and bromine. Chloride of nitryl, analogous to chloride of chlorine, nitrous to hydrochloric, and nitric to hypochlorous acid:

$$\begin{array}{lll} & Cl(NO_2) & ClCl \\ & H(NO_2) & HCl \\ HNO_3 \text{ or } & H(NO_2)O & HClO \end{array}$$

Action of nitric peroxide on hydrocarbons, &c., to produce nitro-compounds, by combination or substitution, after the manner of chlorine and bromine. Conversion, for instance, of amylene $H_{10}C_5$, into $(NO_2)_2H_{10}C_5$, and of naphthalene H_8C_{10}, into $(NO_2)H_7C_{10}$. Production of various nitro-derivatives usually effected by action of nitric acid, as upon naphthalene, for instance:

$$H_8C_{10} + H(NO_2)O = (NO_2)H_7C_{10} + HHO$$

Existence of derivatives with 1, 2, 3, 4 and more atoms of nitryl. General properties of nitro- as of chloro-derivatives similar to those of their originals. Tendency of nitryl like that of chlorine, to intensify acidity, and diminish alkalinity of resulting bodies. Nitro-derivatives characterised by their more or less yellow colour, as in trinitrophenol or picric acid, and, unless very volatile, by their explosibility, as with trinitrocellulose or gun-cotton. Greater or less reduction and reconversion of nitro-derivatives effected by various reducing agents, including more particularly sulphydrate of ammonium, ferrous acetate, and nascent hydrogen.

Nitric chloride, $ClNO_2$; produced by action of dry hydrochloric acid on nitric peroxide, and of phosphoric chloride on nitric acid or nitrates, &c.:

$$Cl_3PO \quad + \quad 3H(NO_2)O \quad = \quad 3ClNO_2 \quad + \quad H_3PO_4$$

A thin pale oil, smelling of aqua-regia and decomposed by water into hydrochloric and nitric acids:

$$HHO \quad + \quad ClNO_2 \quad = \quad HCl \quad + \quad H(NO_2)O$$

NITRATE COMPOUNDS.

Nitrates. Soda-nitre or nitrate of sodium $NaNO_3$, found massive in layers beneath superficial soil in parts of southern Peru. Its purification by solution and crystallisation. Potash-nitre or nitrate of potassium KNO_3, occasionally found massive, as at Cape of Good Hope, but usually disseminated through superficial soil or effloresced upon its surface, as in parts of Bengal. The scrapings, &c., boiled in water, and solution filtered through wood-ashes to decompose any nitrate of calcium. Probable origin of native nitre by oxidation of nitrogenous organic matter, or possibly of ammonia of rain-water (?). Process of nitrification illustrated by saltpetre rot, and artificial nitre beds of Sweden, and nitre walls of Prussia. Exposure to air of waste nitrogenous matter, in presence of weak bases. Nitrates found in juices of plants.

Conversion of soda-nitre into potash-nitre, in gunpowder-works, by its double decomposition with chloride of potassium:

$$NaNO_3 \ + \ KCl \ = \ KNO_3 \ + \ NaCl$$

Resulting common salt removed during evaporation of solution, and potash-nitre crystallised out during cooling of hot liquor. Other nitrates made by dissolving the different metals, their hydrates, oxides, or carbonates, in aqueous nitric acid, and crystallising by evaporation. Solubility of all nitrates in water, with exception of a few basic salts. Consequent non-precipitability of their solutions by any reagent.

Different decompositions of various classes of nitrates by heat. Evolution of oxygen from nitrates of basylous metals to leave nitrites, decomposible at a higher temperature.* Evolution of nitric acid from hydrated nitrates of aluminium and bismuth; and of nitric peroxide and oxygen from nitrates of most heavy metals, leaving metal as silver, protoxide as of lead, and higher oxide as of manganese and iron.

Deflagration of nitrates with combustible matter, mineral or organic. In explosion of gunpowder, charcoal and sulphur burnt by oxygen of nitre. Nitrogen and carbanhydride gases, with some carbonic oxide and hydrogen, liberated at high temperature,—sulphate and carbonate of potassium being left as residue. Decomposition represented approximatively, by equation,

$$8KNO_3 \ + \ S_4 \ + \ C_7 \ = \ 2K_2SO_4 \ + \ 2K_2CO_3 \ + \ N_8 \ + \ 5CO_2?$$

Nitric acid, HNO_3. Its production by various decompositions of all oxides of nitrogen in presence of air and water. Traces formed by combustion of mixture of nitrogen and hydrogen in air, by passing electric sparks through moist mixture of nitrogen and oxygen, &c. The acid usually made by decomposing nitrate of potassium (100 parts) or of sodium (85 parts) with oil of vitriol (100 parts):

$$H_2SO_4 \ + \ NaNO_3 \ = \ NaHSO_4 \ + \ HNO_3$$

Process conducted in glass retort and condenser. Frequent

production of red fumes at beginning and end of operation. Specific gravity of first colourless portion of distillate, and when operating with dry materials, of great bulk of distillate, 1·52, and composition HNO_3. But specific gravity of entire distillate, 1·5, and composition $4HNO_3.H_2O$. Excess of water derived from decomposition of some of the produced nitric acid and acid-sulphate of sodium. Product concentrated when necessary by distillation from oil of vitriol, and freed from nitrous fumes by passage of current of dry carbanhydride gas through heated distillate.

Pure nitric acid HNO_3, a colourless liquid of specific gravity 1·52, freezing at $-55°$, and boiling at $86°$, with partial decomposition. Its vapour-density $\frac{1+14+48}{2}=31·5$. Its decomposition by exposure to sunlight, hygroscopicity, evolution of fumes in moist air, and of heat on admixture with water.

Nitric acid made commercially by distilling nitrate of sodium or potassium with half above quantity of oil of vitriol, in iron cylinders. Distillate passed into series of stoneware bottles, the last containing some water. Reaction effected at two stages:

$$\begin{aligned} H_2SO_4 + 2NaNO_3 &= NaHSO_4 + NaNO_3 + HNO_3 \\ &= Na_2SO_4 + 2HNO_3 \end{aligned}$$

Necessity for increase of temperature to effect second stage of reaction. Colourless, and orange or fuming varieties of nitric acid. The latter made colourless by heating it gently in glass retorts. Specific gravity of colourless commercial acid about 1·42, boiling point 123°, and composition $2HNO_3.3H_2O$, unaltered by distillation. Purification of commercial acid by distillation, rejecting first and last portions, often contaminated with chlorine and sulphuric acid respectively.

Nitric acid possessed of powerfully acid properties. Its reaction with hydrates, oxides, carbonates, &c., to produce nitrates. Most characteristic action of the strong acid that of an oxygenant, from its reduction to state of N_2O_4, N_2O_3, N_2O_2, N_2O, N_2, or NH_3, according to substance acted on and circumstances of experiment.

Solubility of most metals in strong or dilute nitric acid, with

formation of nitrates, and reduction to greater or less extent of excess of acid. Action facilitated by heat, and especially by presence of some nitrous acid or nitric peroxide. Peculiar inertness of strongest colourless acid on tin and iron. Reaction of strong acid on copper to produce the basic nitrate $Cu_2NO_3(HO)_3$.

Violent oxidation of certain elements, as phosphorus, antimony, charcoal, tin, &c., by nitric acid. Its oxidising action on salts and other compounds, illustrated by its conversion of ferrous into ferric salts, of black sulphide into white sulphate of lead, and of white arsenic into arsenic acid. Also by its liberation of iodine from iodide of potassium, and of chlorine from hydrochloric acid. Its oxidation of indigo into isatin, of starch or sugar into oxalic acid, and of turpentine into various products. Its characteristic coloration of morphia, brucia, and woollen cloth.

Its action on various organic bodies, as on naphthalene, cellulose, phenol or carbolic acid, &c. &c., to produce nitro-derivatives. Trinitrophenol or picric acid characterised by a strong yellow colour, whence its formation made use of as a test for nitric acid.

Different modes of testing for nitric acid or nitrates. Nitric acid set free, or brought to state of concentration, by excess of oil of vitriol, and then allowed to act on copper turnings, sulphate of iron, indigo, phenol, &c. Nitrates, including hydric nitrate, also recognised by enabling hydrochloric acid to dissolve gold leaf.

Nitric anhydride, N_2O_5; made by acting with dry chlorine gas on nitrate of silver, heated to about 95°, and then kept at 60°:

$$2AgNO_3 + Cl_2 = 2AgCl + N_2O_5 + O$$

Mixed liquid and solid distillate obtained, the former expelled in current of carbanhydride gas. Occurrence of nitric anhydride as a white, crystalline, unstable, fusible body, volatile at about 45°, with partial decomposition. Its analysis by transmission over ignited copper. Its sharp reaction with water to produce nitric acid:

$$H_2O + N_2O_5 = 2HNO_3$$

Aqua-regia, or nitromuriatic acid. An orange-coloured fuming, corrosive liquid, made by mixing one volume of strong nitric with three of hydrochloric acid. Mixture at first colourless, but becoming gradually darker from decomposition into water, chlorine, and chloro-nitric gas, together with some nitrous chloride:

$$6HCl \quad + \quad 2HNO_3 \quad = \quad 4H_2O \quad + \quad Cl_2 \quad + \quad 2Cl_2NO$$

Solvent action of acid on gold dependent entirely on presence of free chlorine. Similar liquids made by dissolving nitre in hydrochloric, or common salt in nitric acid. Expulsion from its salts and decomposition of either acid by excess of the other.

Chloro-nitric gas, Cl_2NO or $Cl_4N_2O_2$. Compound regarded as a derivative of nitric peroxide NO_2 or N_2O_4, by substitution of chlorine Cl_2, for oxygen O. The chief product of above reaction of hydrochloric and nitric acids upon one another. Red fumes, condensable to volatile liquid, by freezing mixture of ice and salt. Boiling point of liquid $-7°$. Its reaction with water or alkali to form chloride, nitrite, and nitrate of hydrogen or metal:

$$\begin{aligned} \overbrace{H_2O \quad + \quad 2H_2O} \quad + \quad 2Cl_2NO \quad &= \quad H_2O \quad + \quad N_2O_4 \quad + \quad 4HCl \\ &= \quad HNO_3 \quad + \quad HNO_2 \quad + \quad 4HCl \end{aligned}$$

Its immediate decomposition by mercury, and want of action on gold, platinum, &c.

(33.) Phosphorus.

Occurrence of various native phosphates, particularly of phosphate of calcium, $\overset{''}{Ca}_3(PO_4)_2$ or $\overset{''}{Ca}_3P_2O_8$, as coprolite, phosphorite, apatite, &c. Existence of phosphates in primitive rocks, and soils produced by their disintegration. Concentration of phosphorus by plants, particularly in their seeds. Its further concentration by animals, particularly in their bones. Its discharge also by their urine. Its existence in the blood, brain, and various soft tissues of the body in an unoxidised state.

Production of phosphorus by ignition of phosphoric anhydride with charcoal:

$$P_2O_5 \quad + \quad C_5 \quad = \quad 5CO \quad + \quad P_2$$

Preparation of phosphoric anhydride. Bone-ash treated with enough sulphuric acid to remove two-thirds of calcium:

$$Ca''_3P_2O_8 \quad + \quad 2H_2SO_4 \quad = \quad Ca''H_4P_2O_8 \quad + \quad 2Ca''SO_4$$

Syrup of resulting monocalcian phosphate mixed with charcoal, dried, and heated to dull redness. Water thereby driven off, and compound of tricalcian phosphate and phosphoric anhydride left, together with the added charcoal:

$$3Ca''H_4P_2O_8 \text{ or } Ca_3P_2O_8.2H_6P_2O_8 \quad = \quad Ca_3P_2O_8.2P_2O_5 \quad + \quad 6H_2O$$

Residue then strongly ignited in coated earthenware retort, and phosphorus of constituent phosphoric anhydride liberated, distilled off, and condensed in water. Purification of crude product, by fusion under water, and treatment with acid solution of red chromate of potassium, or in other ways.

Phosphorus, a nearly colourless and transparent waxy solid, crystallisable in octa- and dodeca-hedral forms. Its specific gravity 1·82. Its fusion at 44°, into a colourless, transparent, highly refractive oil, capable of being cooled down considerably without solidifying. Its boiling point 290°. Specific gravity of its vapour 62, instead of 31, even at 1000° C. Consequent representation of molecule of phosphorus by symbol P_4. Similar anomaly in vapour-density of arsenic, and representation of its molecule by symbol As_4. Slight volatilisation of phosphorus at ordinary temperatures. Its considerable volatilisation in current of steam. Free solubility of phosphorus in trichloride of phosphorus, disulphide of carbon, and chloride of sulphur. Its more sparing solubility in hydro-carbons, volatile and fixed oils, ether, &c.

Inflaming point of phosphorus in air, about 50°. Its ready inflammability by friction. Slow oxidation and consequent luminosity of phosphorus in air at ordinary temperatures, often

leading to its spontaneous combustion. Its want of luminosity in oxygen, unless rarefied. Interference of ether-vapour, &c., with its luminosity in air.

Production of suboxide of phosphorus (?), and phosphorous and phosphoric anhydrides, P_2O_3 and P_2O_5, by burning phosphorus in dry air. Brilliant combustion of phosphorus in oxygen gas. Its direct combination with sulphur, chlorine, bromine, and iodine; also with many of the metals to form phosphides. Its conversion into phosphorous and phosphoric acids, H_3PO_3 and H_3PO_4, by action of nitric acid and similar oxygenants. Its reduction of various metallic solutions, with precipitation of metal. Its reaction with water and alkaline liquids, to produce phosphoretted hydrogen gas and hypophosphorous and phosphorous acids or salts.

Various allotropic states of phosphorus. Amorphous phosphorus prepared commercially by Schrötter's process of heating ordinary phosphorus for some hours to temperature of 230°—250°, out of access of air. Chocolate-red, or even vermillion-red lump or powder. Its specific gravity 2·14. Its fusion at 250°—260° with reconversion into ordinary phosphorus. Its insolubility in disulphide of carbon, &c. Its non-oxidisability by exposure to dry air, and non-inflammability below 260°. Its insolubility in solutions of caustic alkali. Brodie's process for preparing amorphous phosphorus by means of iodine. Series of combinations and decompositions of iodine and phosphorus, whereby conversion of indefinite quantity of phosphorus effected by small quantity of iodine. Retention of minute proportion of iodine in the product, whence its capability of being sublimed like metallic arsenic, without fusion or reconversion. Its specific gravity 2·23. Its correspondence to the electro-positive or insoluble variety of sulphur (?).

(34.) Phosphine,

Or phosphoretted hydrogen, H_3P. Existence of spontaneously and non-spontaneously inflammable varieties of the gas. Its formation by various reductions of hypophosphorous and phosphorous acids, H_3PO_2 and H_3PO_3; and of phosphoric acid

H_3PO_4, by means of potassium. Also, by metamorphosis of aqueous hypophosphorous and phosphorous acids, at a boiling heat:

$$4H_3PO_3 = 3H_3PO_4 + H_3P$$

Its usual production by reaction of phosphorus with heated solution of caustic alkali:

$$3KHO + 3H_2O + P_4 = 3KH_2PO_2 + H_3P$$

Also by action of water or acids on certain phosphides, as of calcium:

$$6HCl + Ca_3P_2 = 3CaCl_2 + 2H_3P$$

A sparingly soluble, neutral, condensable gas, having a very offensive garlic odour. Its specific gravity $\frac{3+31}{2} = 17$.

Its inflammability, usually spontaneous. Its deoxidising action on hypochlorous acid and salts, nitric acid, gold and silver salts, &c. &c. Combinations of sulphur and the halogens with its hydrogen, and, if in excess, with its phosphorus also. Combinations of various heated metals with its phosphorus,—hydrogen being liberated. Its absorption by metallic solutions, as of cupric sulphate, usually with formation of phosphide:

$$3CuSO_4 + 2H_3P = 3H_2SO_4 + Cu''_3P_2$$

Analogy of phosphoretted hydrogen to ammonia, shown particularly by its ethyl-derivatives and their salts. Formation of crystalline hydriodate of phosphine, or iodide of phosphonium, PH_3HI, by heating iodine in current of dry phosphoretted hydrogen, and in other ways. A colourless, fusible, volatilisable salt, crystallising in deliquescent cubes.

Spontaneous inflammability of certain varieties of phosphine due to their containing a small proportion of the vapour of a liquid phosphide of hydrogen, condensable by cold of ice and salt, and decomposible by action of strong hydrochloric acid into a solid phosphide, and gaseous phosphine. Similar decomposition of the vapour by its exposure to sunlight.

(35.) Phosphine Derivatives, &c.

Phosphorous chloride, or trichloride, Cl_3P. A heavy volatile liquid, made by action of dry chlorine on phosphorus, preferably dissolved in disulphide of carbon. Its boiling point 74°. Its solution of phosphorus, and solubility in benzol, disulphide of carbon, &c. Its rapid absorption of chlorine to form the pentachloride, and slow absorption of oxygen at boiling heat to form the oxichloride. Its decompositions by water and ammonia, to form phosphorous acid and amide respectively, similar to those of the oxichloride. The pentachloride, Cl_5P; made by action of excess of dry chlorine on phosphorus, preferably dissolved in the trichloride. A yellow crystalline mass, volatile below 100°, and fusible only under pressure. Correspondence of its vapour to 4 volumes, owing to dissociation into Cl_3P (2 vols.), and Cl_2 (2 vols.). Its reaction with water, &c., to yield the oxichloride, and with sulphuretted hydrogen to yield the sulphochloride. Its frequent employment in organic chemistry, to transform oxides into chlorides, by its own conversion into oxichloride.

Phosphoric chloride, or oxichloride, Cl_3PO; a heavy volatile liquid, made by reaction of the pentachloride on water and various hydrates, hydrylates, and oxides:

$$Cl_5P \quad + \quad H_2O \quad = \quad 2HCl \quad + \quad Cl_3PO$$

Its boiling point 110°. Its decompositions by water and ammonia respectively, with exchange of chlorine for hydroxyl and amidogen, to form phosphoric acid H_3PO_4, and phosphoric amide H_6PON_3, respectively:

$$\begin{array}{lllll} Cl_3PO & + \quad 3HHO & = \quad 3HCl & + \quad (HO)_3PO \\ Cl_3PO & + \quad 3HH_2N & = \quad 3HCl & + \quad (H_2N)_3PO \end{array}$$

In last reaction, resulting hydrochloric acid produced in form of sal-ammoniac. Sulphochloride of phosphorus Cl_3PS very similar to the oxichloride, not readily decomposible by water, but yielding a sulphoxiphosphate Na_3PSO_3, with caustic alkali:

$$Cl_3PS \quad + \quad 3\mathit{NaNaO} \quad = \quad 3NaCl \quad + \quad (NaO)_3PS$$

The compounds of phosphorus with bromine, similar to those with chlorine. The iodides, made by dissolving atomic proportions of phosphorus and iodine in disulphide of carbon, and evaporating down. The tris-iodide I_3P, unstable and not well defined. The din-iodide I_2P or I_4P_2, a bright red, perfectly definite, crystalline compound, melting at 110°, and, like the chlorine compounds, much used in organic chemistry.

The metallic phosphides comparatively unimportant compounds, mostly referrible to the types $\overset{''}{M}_3P_2$ and $\overset{''}{M}_2P_2$, corresponding to the iodides I_3P and I_4P_2. Heavy metal phosphides obtained by heating the melted metals with phosphorus; or by acting on the metals, their oxides, or salts, with phosphoretted hydrogen. Phosphides of alkali-earth-metal, as of calcium, made by passing the vapour of phosphorus over the ignited oxides, so as to produce mixtures of phosphide and phosphate. These phosphides decomposed by water and dilute acids, with evolution of phosphoretted hydrogen.

(36.) Oxides, Sulphides, and Acids of Phosphorus.

Composition of normal oxides and sulphides of phosphorus:

P_2O	Hypophosphorous	P_2S
P_2O_3	Phosphorous	P_2S_3
P_2O_5	Phosphoric	P_2S_5

Absence of oxide P_2O, and existence of additional oxides and sulphides P_4O, P_4S, and P_2S_{12}. Acids and salts of phosphorus:

H_3PO_2	Hypophosph.	KH_2PO_2
H_3PO_3	Phosphorous	K_2HPO_3
H_3PO_4	Phosphoric	K_3PO_4

Gradually increasing basicity of acids with oxygenation. Their metamorphic relations with one another, and with phosphoretted hydrogen H_3P. Missing member of the series, H_3PO, represented by Cl_3PO, Et_3PO, &c.

Relationship of chlorides to acids, as of Cl_3PO to $(HO)_3PO$,

vide supra. Relationship of anhydrides to acids, that of oxides to hydrates:

$$3H_2O + P_2O_3 = 2H_3PO_3$$
$$3H_2O + P_2O_5 = 2H_3PO_4$$

Hydrations expressible with water-type formulæ, thus:

$$\left.\begin{matrix}H_3\\H_3\end{matrix}\right\}O_3 + \left.\begin{matrix}PO\\PO\end{matrix}\right\}O_3 = \left.\begin{matrix}H_3\\PO\end{matrix}\right\}O_3 + \left.\begin{matrix}H_3\\PO\end{matrix}\right\}O_3$$

The normal sulphides of phosphorus, P_2S, P_2S_3, and P_2S_5, made by heating together atomic proportions of phosphorus and sulphur, in atmosphere of carbanhydride. Perfectly definite, volatile, crystallisable compounds, decomposible by water with evolution of sulphuretted hydrogen; but soluble in solutions of alkaline sulphide or sulphydrate, to form sulpho-hypophosphites, -phosphites, and -phosphates respectively. The last salts dimetallic only, as Na_2HPS_4. The sulphoxiphosphates trimetallic, as Na_3PSO_3; *vide supra.*

Suboxide of phosphorus P_4O (?), an orange-red mass or powder, formed during combustion of phosphorus in air, passage of oxygen on to phosphorus under water, &c. Probably impure amorphous phosphorus. Leverrier's suboxide a flocculent, canary-yellow precipitate, made by exposing pieces of phosphorus moistened with trichloride of phosphorus to the air, dissolving crude yellow product in water, and boiling the solution.

HYPOPHOSPHOROUS COMPOUNDS.

Hypophosphites. Mono-metallic salts, made, together with phosphoretted hydrogen, by heating phosphorus in solutions of alkali or alkali-earth, and evaporating down; also by double decomposition with one another. For the most part crystallisable, inflammable salts, tolerably permanent when dry. Oxidisability on exposure to air, and reducing action, of hypophosphite solutions. Their decomposition, when boiled with strong alkali, into phosphate and hydrogen:

$$2KHO + KH_2PO_2 = K_3PO_4 + H_4$$

Hypophosphorous acid H_3PO_2, made by precipitating barium-salt with sulphuric acid, or lead-salt with sulphuretted hydrogen. A viscid liquid, decomposed by heat into phosphoric acid and phosphine:

$$2H_3PO_2 = H_3PO_4 + H_3P$$

Its reduction by nascent hydrogen to state of phosphine; and oxidation by exposure to air into phosphorous and phosphoric acids. Its reducing action on salts of gold, silver, mercury, permanganic acid, &c. &c. Its peculiar action on salts of copper, to produce red-brown deposit of cuprous hydride CuH, or Cu_2H_2.

PHOSPHOROUS COMPOUNDS.

Phosphorous anhydride P_2O_3, an imperfectly known substance, made by burning phosphorus with deficit of air. Its occurrence in the form of volatile white flakes, possessing a garlic odour, and rapidly absorbing moisture to form phosphorous acid.

Phosphorous acid H_3PO_3, producible in various ways, as in exposure of sticks of phosphorus to moist air; best made by decomposing phosphorous chloride with water (passing chlorine through excess of melted phosphorus under water), and expelling hydrochloric acid by evaporation.

A crystalline mass, or thick syrupy liquor, decomposible by heat with evolution of phosphine, reducible to state of phosphine by nascent hydrogen, oxidisable into phosphoric acid by exposure to air, and reductive of salts of gold, silver, mercury, &c., and of permanganic acid only after some time.

Phosphites. Di-metallic and mono-metallic salts, M'_2HPO_3 and $M'H_2PO_3$, of but little general interest; made by neutralising the acid with bases and crystallising, or by double decomposition with one another. Decomposition of salts by heat, with evolution of hydrogen or phosphoretted hydrogen. Their solutions readily oxidisable, but not decomposible by ebullition with caustic alkali.

PHOSPHORIC COMPOUNDS.

Phosphoric anhydride P_2O_5, made by burning phosphorus in dry air or oxygen. A snow-white, amorphous, flocculent solid, fusible at a red, and volatile at a stronger heat. Inodorous when pure, and without action on litmus paper. Its extreme deliquescence, and important uses as a desiccating agent. Its expulsion of more volatile anhydrides from acids and salts, at different temperatures. Its decomposition, by ignition with charcoal, to yield phosphorus.

Phosphoric, or orthophosphoric acid H_3PO_4, a well-defined, soluble, crystallisable compound, producible by many reactions.

Its formation from phosphorus, by oxidising the element with nitric acid and evaporating down; or by dissolving the anhydride in boiling water.

Its manufacture for commercial purposes, by treating bone-ash with sulphuric acid:

$$3H_2SO_4 \quad + \quad \overset{\prime\prime}{Ca}_3(PO_4)_2 \quad = \quad 3\overset{\prime\prime}{Ca}SO_4 \quad + \quad 2H_3PO_4$$

Purification of crude acid, if necessary, in various ways; as by neutralising it with ammonia, igniting ammonia salt, and dissolving the residue (metaphosphoric acid) in boiling water.

Occasional production of phosphoric acid by treating precipitate of phosphate of lead, thrown down from phosphate solutions by acetate or nitrate of lead, with sulphuretted hydrogen:

$$3H_2S \quad + \quad \overset{\prime\prime}{Pb}_3(PO_4)_2 \quad = \quad 3PbS \quad + \quad 2H_3PO_4$$

Occurrence of orthophosphoric acid in form of hard transparent crystals, by allowing thin syrup to stand in vacuo over oil of vitriol. Its solubility in water to form a strongly acid and stable liquid, expelling the more volatile acids from their salts, and dissolving the basylous metals with evolution of hydrogen. Action of heat upon ortho-acid, *vide infra*. Its non-precipitation of albumin.

Phosphates, or orthophosphates. The phosphoric a tribasic acid forming primary, secondary, and tertiary salts and ethers. Illustrative salts:

KH_2PO_4	Potassium phosphate } or acid phosphates of potassium
NaH_2PO_4	Mono-sodium phosphate } and sodium
Na_2HPO_4	Di-sodium phosphate, or neutral phosphate of sodium
$(NH_4)_2HPO_4$	Di-ammonium phosphate, or neutral phosphate of ammonia
$(NH_4)NaHPO_4$	Sodio-ammonium phosphate, or microcosmic salt
Na_3PO_4	Tri-sodium phosphate, or alkaline phosphate of sodium
Ag_3PO_4	Tri-argentian phosphate, or yellow phosphate of silver
$(NH_4)Mg''PO_4$	Ammonio-magnesian, or triple phosphate
$Fe'''PO_4$	Ferric normal phosphate
$Ca''_3(PO_4)_2$	Tri-calcian phosphate, or bone-earth

Occurrence of primary phosphates as soluble acid compounds. Their production by addition of phosphoric or other acid to secondary and tertiary phosphates. Those of alkali- and alkaline earth metals crystallisable. Those of heavy metals known only in solution.

Of secondary phosphates, those of the alkali-metals, well-defined crystalline salts, soluble in water, forming neutral or somewhat alkaline solutions. Their production by neutralising crude phosphoric acid (from bone-ash) with carbonates. Microcosmic salt made by boiling together solutions of common di-sodium phosphate and sal-ammoniac:

$$Na_2HPO_4 + NH_4Cl = NH_4NaHPO_4 + NaCl$$

Other secondary phosphates, unstable and little known compounds.

Of tertiary phosphates, those of the alkali-metals alone soluble in water, forming strongly alkaline solutions. Their production by addition of caustic alkali to secondary phosphates, and crystallisation. Their instability, and decomposition even by carbonic acid of the air. Other tertiary phosphates insoluble compounds, made by double decomposition or found native. Production of free acid during precipitation of tertiary phosphates of heavy metal by secondary phosphates of alkali-metal:

$$Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + \overbrace{2NaNO_3 + HNO_3}$$

Native phosphates very numerous, and some of them very complex. Those of calcium, lead, and magnesium associated with fluorides or chlorides in apatite $Ca_5(PO_4)_3F$, polymorphite $\overset{''}{P}b_5(PO_4)_3F$, and wagnerite $\overset{''}{M}g_2(PO_4)F$, respectively. That of aluminium basic in turquoise, wavellite, &c.

Phosphoric acid and phosphates recognised by giving yellow precipitate with nitric acid solution of molybdate of ammonia; white precipitate with nitric acid solution of bismuth nitrate, and brownish precipitate with acetic acid solution of ferric acetate. Precipitation of silver salts yellow, and of barium salts white, by phosphates, but not by phosphoric acid. Their precipitation of ammoniacal solutions of magnesium salts.

METAPHOSPHATE COMPOUNDS.

Production of metaphosphate of sodium by ignition of monosodium orthophosphate, or of microcosmic salt:

$$NaH_2PO_4 = NaPO_3 + H_2O$$

Production of gelatinous metaphosphates of lead and silver by double decomposition:

$$NaPO_3 + AgNO_3 = AgPO_3 + NaNO_3$$

Metaphosphoric acid formed in solution, by decomposing sodium-salt with acetic acid, or lead-salt with sulphuretted hydrogen:

$$Pb''(PO_3)_2 + H_2S = 2HPO_3 + PbS$$

Its formation, by ignition of orthophosphoric acid, as a glassy mass, fusible and volatilisable by heat, very deliquescent, and soluble without change in cold water:

$$H_3PO_4 - H_2O = HPO_3$$

Distinctive precipitation by metaphosphoric acid of albumin; and, without its prior neutralisation, of silver- (transparent, white) and barium-salts.

Conversion of acid and salts into ortho-compounds by boiling in water, or prolonged solution.

Production of meta- or ortho-acid according to temperature, by reaction of anhydride with water:

$$H_2O + P_2O_5 = 2HPO_3$$

Metaphosphoric acid and salts regarded as anhydro-compounds:

$$3NaPO_3 = Na_3PO_4.P_2O_5$$

Salts consequently made by treating orthophosphates with phosphoric or other anhydride. Reduction of two-thirds of constituent phosphorus (*i.e.* the phosphoric anhydride) of metaphosphates, as of metaphosphate of calcium, by ignited charcoal.

Polymeric varieties of metaphosphates.

PYROPHOSPHATE COMPOUNDS.

Production of pyrophosphate of sodium by igniting di-sodium orthophosphate;

$$2Na_2HPO_4 = Na_4P_2O_7 + H_2O;$$

and of lead and silver pyrophosphates by double decomposition:

$$Na_4P_2O_7 + 2Pb(NO_3)_2 = Pb_2P_2O_7 + 4NaNO_3$$

Production of pyrophosphoric acid in solution by decomposing lead-salt with sulphuretted hydrogen:

$$Pb_2P_2O_7 + 2H_2S = H_4P_2O_7 + 2PbS$$

Also, as a soft glass, or in semi-crystalline masses, by heating the ortho-acid to 215°:

$$2H_3PO_4 - H_2O = H_4P_2O_7$$

Distinctive property of pyrophosphoric acid to give no precipitate with albumin, and only after neutralisation, a chalky white precipitate with nitrate of silver.

Ultimate conversion of aqueous pyrophosphates of metal and hydrogen into the ortho-compounds. No direct metamorphic relation between pyrophosphoric acid and phosphoric anhydride. Pyrophosphoric, probably a compound of the ortho- and meta-acids, and decomposible into the two. Its tetra-basicity shown in various ways. Other intermediate compounds.

The phosphorous and phosphoric amides, very numerous and complex bodies, made by acting on the different chlorides and anhydrides with ammonia, under various circumstances. Existence of phosphotriamide $(H_2N)_3PO$, phospho-diamic acid $HO(H_2N)_2PO$, and phosphamic acid $(HO)_2H_2NPO$, all deriving from phosphoric acid $(HO)_3PO$. Also of a similar series of pyrophosphoric amides. Pyrophospho-diamic acid $(HO)_2(H_2N)_2P_2O_3$, in particular, a comparatively stable body, formed under great variety of circumstances. Existence of many other correlated nitrogen compounds of phosphorus, some of them containing chlorine, as the chloronitride $Cl_2N''P$, and chlorophosphamide $(H_2N)_2Cl_3P$, both analogous to the pentachloride Cl_5P.

(37.) Arsenic, Antimony, and Bismuth.

Relationship of arsenic and antimony to phosphorus, analogous to that of selenium and tellurium to sulphur. Bismuth further removed from phosphorus, and more basylous, fixed, and metallic than its congeners. The hydrides, H_3As and H_3Sb, similar in constitution and properties to H_3P. The hydride of bismuth non-existent, but represented by the ethide Et_3Bi, a volatile liquid closely resembling its analogues Et_3Sb, Et_3As, and Et_3P. The chlorides, Cl_3P, Cl_3As, Cl_3Sb and Cl_3Bi, similar volatile compounds decomposible by water. The oxides, As_2O_3, Sb_2O_3, and Bi_2O_3, and the sulphides, As_2S_3, Sb_2S_3, and Bi_2S_3, also very similar to one another, and to the corresponding phosphorus compounds. Those of arsenic and antimony decidedly stylous, forming definite salts with oxi- and sulpho-bases. Those of bismuth neutral or basylous. Formation by each element of

incomplete series of penta-compounds, such as arsenic anhydride and acid, As_2O_5 and H_3AsO_4, antimonic chloride Cl_5Sb, bismuthic peroxide Bi_2O_5, &c. Very general isomorphism of phosphates with arseniates, and of arsenious with antimonious and bismuthous compounds. Existence of both ortho- and meta-compounds, as of antimony, instanced by native sulphantimonites of silver, Ag_3SbS_3 red-silver, and $AgSbS_2$ myargyrite.

(38.) Boron.

Symbol, B; atomic weight, 11. A triad non-metallic element. Its hydride unknown, but represented by boric tri-ethide Et_3B, trifluoride F_3B, trichloride Cl_3B, &c. Reaction of chloride with water to form trihydrate, or boracic acid, $(HO)_3B$ or H_3BO_3. Existence of metaboric acid HBO_2, and metaborates. Also of boric oxide or anhydride B_2O_3:

$$H_3BO_3 - H_2O = HBO_2$$
$$2H_3BO_3 - 3H_2O \text{ or } 2HBO_2 - H_2O = B_2O_3$$

Occurrence of boron as boracic acid in Tuscany, as tincal or borax in Thibet, as boracite at Stassfurth in Prussia, and as borocalcite and boronatro-calcite in Ecuador and South America. Its existence in small proportion in many other minerals, as tourmaline.

Preparation of boron from borofluoride of potassium, by its ignition with potassium or sodium:

$$2KF_4\overset{'''}{B} + K_6 = 8KF + \overset{'''}{B}_2$$

Also by ignition of boric anhydride with sodium:

$$Na_6 + B_2O_3 + 3B_2O_3 = B_2 + 3(Na_2O.B_2O_3) \text{ or } 6NaBO_2$$

An amorphous, soft, olive-brown powder, soiling the fingers. Its slight solubility in pure, and insolubility in saline water. Its direct combination with chlorine, oxygen, sulphur, and nitrogen; and liberation of hydrogen from hydrochloric acid, steam, sulphuretted hydrogen, and ammonia, at a red heat. Its oxidation

by fusion with hydrate, carbonate, acid-sulphate, and nitrate of potassium, and by ebullition with sulphuric, nitric, and nitro-hydrochloric acids.

Its increase of density and loss of activity after prolonged ignition. Its fusion at an intense heat. Its non-conductivity of heat and electricity.

Adamantine boron produced by exposing aluminium and boric anhydride to an intense heat for some hours:

$$B_2O_3 \quad + \quad Al_2 \quad = \quad Al_2O_3 \quad + \quad B_2.$$

Or by strongly heating aluminium with preformed boron, in enclosed charcoal crucible. Dissolution of reduced boron in the melted metal, and its crystallisation therefrom on cooling. Adamantine crystals picked out from residue left by dissolving away aluminium with hydrochloric acid. Short quadratic octahedrons, varying from scarcely appreciable yellow to deep garnet-red, or almost black colour, lustrous and highly refractive, of specific gravity 2·63, and harder than corundum.

Adamantine, unlike amorphous form of boron, infusible in oxihydrogen blow-pipe; incombustible in air, and scarcely combustible in oxygen, though combustible in chlorine; not appreciably acted on by boiling nitric acid, or by fused nitre. Reaction of both forms of boron with ignited platinum, to form fusible compounds.

Production, together with adamantine boron, of opaque micaceous scales, or thin hexagonal plates, having dark lustrous aspect and coppery red tinge of colour. Same substance obtained by passing chloride of boron vapour over melted aluminium, and in other ways. Its composition represented by formula Al_2B_4. Compound formerly described as graphitic boron. Its combustibility in chlorine and solubility in nitric acid, but indifference to most chemical agents.

(39.) Halogen Compounds of Boron.

Fluoride of boron F_3B, made by heating boric oxide and fluor-spar in a gun-barrel :

$$3F_2Ca \quad + \quad B_2O_3 \quad + \quad 3B_2O_3 \quad = \quad 2F_3B \quad + \quad 3(CaO.B_2O_3), \text{ or } 3Ca''B_2O_4$$

Also, by acting on boric oxide with hydrofluoric acid, or a mixture of sulphuric acid and fluor-spar:

$$3H_2SO_4 \quad + \quad 3F_2Ca \quad + \quad B_2O_3 \quad = \quad 3Ca''SO_4 \quad + \quad 2F_3B \quad + \quad 3H_2O$$

A gas of sp. gr. $\frac{57+11}{2} = 34$, incombustible, corrosive, and fuming in air. Direct combination of equal volumes of boric fluoride and ammonia, to form a white, opaque, volatile solid $H_3N.F_3B$. Solubility of 700 vols. of boric fluoride in 1 vol. of water, to form dense oily liquid, $3H_2O.2F_3B$. Existence also of more stable volatilisable compound $4H_2O.2F_3B$.

Hydrofluoboric acid, HF_4B or $HF.F_3B$, a compound known only in solution, made, with precipitation of boracic acid, by passing gaseous fluoride of boron into excess of water:

$$4F_3B \quad + \quad 3H_2O \quad = \quad 3HF_4B \quad + \quad H_3BO_3$$

Also, by dissolving boric acid or oxide in aqueous hydrofluoric acid:

$$4HF \quad + \quad H_3BO_3 \quad = \quad HF_4B \quad + \quad 3H_2O$$

The fluoborides, or borofluorides, as KF_4B, or $KF.F_3B$, for the most part well defined, sparingly soluble, crystallisable, fusible salts, decomposing into constituent fluorides at a stronger heat. Their production by neutralising hydrofluoboric acid, or by equivalent processes. Great tendency to formation of these compounds, shown by reaction of boracic acid and fluoride of potassium, with co-production of caustic potash :

$$4KF \quad + \quad H_3BO_3 \quad = \quad KF_4B \quad + \quad 3KHO$$

Choride of boron Cl_3B, best made by combination of boron with dry chlorine at a moderate heat. Producible by heating a mixture of boric oxide and charcoal in current of chlorine, or by heating boron in hydrochloric acid gas, &c. A heavy fuming liquid, boiling at 17°. Sp. gr. of vapour $\frac{106\cdot5+11}{2} = 58\cdot7$. Its direct union with ammonia to form a white volatile solid $3H_3N.2Cl_3B$. Its reaction with water, alcohol, &c., to form boric hydrate, ethylate, &c.:

$$Cl_3B + 3HHO = 3HCl + H_3BO_3 \text{ or } (HO)_3B$$

(40.) Boracic Acid.

The acid obtained chiefly from suffioni of volcanic district of Tuscany. Issue of heated gas, with steam and mineral matter, through earth-fissures or borings, into ponds or lagoons, natural or artificial. Gradual charging of water with boracic acid to extent of one-half per cent. or so, by its flow through series of six or eight lagoons, each surrounding two or three suffioni. Solution then evaporated to crystallising point, in leaden pans several hundred feet long, by natural heat of suffioni. Crude acid purified by recrystallisation, or by conversion into borax and crystallisation.

Precipitation of boracic acid by acidifying hot concentrated solution of borax with hydrochloric or sulphuric acid, and recrystallising:

$$\underbrace{2NaH_5B_2O_6} + H_2SO_4 = 4H_3BO_3 + Na_2SO_4$$

Occurrence of boracic acid H_3BO_3, in white nacreous scales, of sp. gr. 1·48, sparingly soluble in cold, freely soluble in hot water, and in alcohol. Its volatilisation in vapour of water or alcohol. Its property of communicating a green colour to the flame of alcohol. Its slightly acid taste, and reaction with litmus paper. Its capability both of decomposing dissolved carbonates, and of being liberated by carbonic acid. Its action as a base.

Correspondence of tartarised borax $KBO_2\overline{T}$, to tartar-emetic $KSbO_2\overline{T}$. Browning of turmeric paper by boracic acid solution allowed to evaporate on it, or in presence of strong hydrochloric acid, &c.

Metaboric acid HBO_2, $= H_3BO_3 - H_2O$, a pulverulent substance obtained by heating orthoboric or boracic acid to temperature of 120°.

Boric oxide, or anhydride B_2O_3, obtained in pulverulent state by further heating ortho- or meta-boric acid. Its fusibility below a red heat into transparent viscid liquid, solidifying into a transparent glass of sp. gr. 1·83. Its absorption of moisture from the air to reproduce boracic acid. Its employment as a flux in metallurgy. Its expulsion, at a red heat, of more volatile anhydrides from their salts. Its volatility at an intense heat, and use in the artificial production of crystalline minerals.

Borates. General formula of orthoborates M_3BO_3. Salts illustrated by boracic ethers, &c., and products of fusion of boric oxide with hydrates of sodium and barium, oxide of magnesium, &c. Probable identity of acid or hydrogen orthoborates with hydrated meta-borates. (?)

Ordinary borates or meta-borates represented by general formula $x MBO_2$, and typified by borates of sodium. Tendency to formation of multiple salts.

Normal salt	$Na_4B_4O_8 . 16H_2O$
Borax	$Na_2H_2B_4O_8 . 9 \& 4H_2O$
Tri-acid salt	$Na H_3B_4O_8 . 7H_2O$

Borates of alkali-metal alone decidedly soluble in water. Want of neutrality, and increase in alkalinity by dilution, of their solutions, owing to decomposition.

Common borax or disodio-tetraborate found native as tincal. Produced by spontaneous evaporation of lake waters of Thibet. Imported in skins, and purified from grease, &c., by washing with caustic soda and recrystallising.

Artificial borax made by dissolving Tuscan boracic acid in boiling carbonate of sodium solution, or preferably by fritting

acid with soda ash in reverberatory furnace, lixiviating and evaporating down solution. Also by boiling boracite, boronatrocalcite, &c., with carbonate of sodium.

Occurrence of borax in large flattened six-sided or rectangular prisms, with 9 atoms of water of crystallisation, doubtfully efflorescent, and soluble in half their weight of boiling water. Its occurrence also in octahedrons with 4 atoms of water, when deposited at temperatures not below 130°, from dense solutions containing large excess of sodium-carbonate. The tetrahydrated salt possibly an ortho-borate:

$$Na_2H_2B_4O_8 . 4H_2O \quad = \quad 2NaH_5B_2O_6$$

Effect of heat on borax, to drive off water with intumescence, leaving fused anhydro-salt or calcined borax:

$$Na_2H_2B_4O_8 \quad - \quad H_2O \quad = \quad Na_2B_4O_7 \quad \text{or} \quad Na_2B_2O_4.B_2O_3$$

Solubility of metallic oxides in fused anhydro-salt. Hence its value as a blowpipe reagent, and for soldering. Its employment also as a flux.

Normal metaborate of sodium $NaBO_2.4H_2O$, or $Na_4B_4O_8.16H_2O$, made by fusing ordinary borax with carbonate of sodium and crystallising. Tri-acid or monosodio-tetraborate $NaH_3B_4O_8.7H_2O$, made by boiling solutions of borax and sal-ammoniac:

$$Na_2H_2B_4O_8 \quad + \quad NH_4Cl \quad = \quad NaH_3B_4O_8 \quad + \quad NaCl \quad + \quad NH_3$$

Existence of yet more highly acid borates. General correspondence of potassium and ammonium borates to those of sodium.

Borate of magnesium $Mg''B_2O_4$, found native as boracite, in regular dodecahedrons analogous to spinelle $Mg''Al_2O_4$, and in amorphous state. Partial replacement of oxygen by chlorine, in some specimens, as $Mg_4B_8(O_{15}Cl_2)$.* Borate of calcium $Ca''H_2B_4O_8.2H_2O$, found native as borocalcite; and double borate of calcium and sodium $NaCa''H_3B_6O_{12}.6H_2O$, as boronatrocalcite.

* $Mg_4B_8O_{16} \quad = \quad 4MgB_2O_4$

Most other borates more or less unstable, indefinite, insoluble compounds, procured by precipitation; and dissolved, with decomposition, by most acids.

Sulphide of boron B_2S_3, made by heating boron in sulphur vapour, or mixture of boric oxide and lamp-black in disulphide of carbon vapour, &c. A white solid body, having a pungent irritating odour, and volatilising in a stream of sulphuretted hydrogen. Its decomposition by water, with production of sulphydric and boracic acids:

$$B_2S_3 + 6H_2O = 3H_2S + 2H_3BO_3$$

Nitride of boron BN, or B_3N_3, produced during ignition of boron in air or nitric oxide, and in other ways. Best obtained by heating boron in nitrogen or ammonia; or by igniting borax, or, preferably, normal borate of sodium, with sal-ammoniac, and washing residue:

$$NaBO_2 + NH_4Cl = 2H_2O + NaCl + NB$$

A white, amorphous, insoluble, infusible, and non-volatile powder. Its decomposition, when heated in a current of steam, into boracic acid and ammonia:

$$NB + 3H_2O = H_3N + H_3BO_3$$

(41.) Gold and Triad Metals.

Boron without well recognised metallic analogues. Possible association with it of aluminium; symbol, Al; atomic weight, 27·5. Formula of aluminium chloride Cl_3Al, or Cl_6Al_2; of the sodio-chloride $NaCl_4Al$; of cryolite Na_3F_6Al; of corundum Al_2O_3; of spinelle $MgAl_2O_4$, &c.

Thallium; symbol Tl; atomic weight 203; monadic in its best known combinations, but triadic in thallic chloride Cl_3Tl, nitrate $(NO_3)_3Tl$, &c. Resemblance of thallous hydrate TlHO, to that of potassium in solubility, causticity, and absorption of

carbanhydride, but not in resistance to heat. Resemblance also of thallous perchlorate, acid-tartrate, platino-chloride, and alumino-sulphate to similar compounds of potassium. Resemblance however of insoluble thallous sulphide Tl_2S, iodide TlI, and chloride TlCl, to analogous silver compounds.

Gold; symbol Au; atomic weight 196; triadic in its best known combinations, as auric chloride Cl_3Au, potassium-aurate $KAuO_2.3H_2O$, &c. Acidulous character of gold in auric compounds. Existence also of well defined monad gold compounds, as aurous iodide AuI, sodio-sulphide $NaAuS.4H_2O$, sodio-hyposulphite $Na_3Au(S_2O_3.H_2O)_2$, &c. &c.

CHAPTER V.

(42.) Carbon Elements.

Carbon—Silicon, Tin, Lead.

Tetrad character of elements shown by their combining with hydrogen, ethyl, fluorine, chlorine, &c., in proportion of one atom to four. Their symbols and atomic weights. Comparison of carbon and nitrogen series of elements:

Carbon	C	12	N	14
Silicon	Si	28	P	31
?	?	72	As	75
Tin	Sn	118	Sb	122
Lead	Pb	207	Bi	208

Existence of unsaturated or diad combinations of above elements, illustrated by carbonous oxide CO; by stannous oxide SnO, and chloride Cl_2Sn; and by lead oxide PbO, chloride Cl_2Pb, and lead-salts in general. Carbon the characteristic element of organic bodies. Number, variety, and complexity of its compounds with hydrogen, oxygen, and nitrogen.

(43.) Silicon.

Its extensive distribution in nature. Silica, or oxide of silicon, alone or in form of divers silicates, the most abundant solid constituent of the earth's crust. Occurrence of crystallised silica as quartz, rock-crystal, sand, &c., and of amorphous silica, as calcedony, flint, opal, &c. Felspar, or double silicate of aluminium and potassium, the chief constituent of most primitive rocks. Other abundant silicates met with as serpentine, chlorite,

mica, hornblende, &c. Silicate of aluminium the basis of clay and porcelain. Occurrence of much dissolved silica in water of Geyser springs. Existence of silica in vegetable kingdom, especially in stems of cereals, bamboos, &c., and in skeletons of diatoms, &c.

I Silicon, in amorphous state, made by passing chloride of silicon vapour over heated sodium, or preferably by heating silicofluoride of potassium with sodium:

$$K_2F_6Si'''' + Na_4 = 2KF + 4NaF + Si''''$$

A soft dull-brown powder, soiling the fingers, insoluble in, and heavier than water, non-conductive of electricity, &c. Its solubility in hot potash, aqua-regia, and hydrofluoric acid. Its combustibility in air or oxygen, and oxidation by fused hydrate, carbonate, and nitrate of potassium, &c. Its increase of density and loss of activity after strong ignition, shown by its sinking in oil of vitriol, and not burning in oxygen, or dissolving in hydrochloric acid. Solubility of dense silicon in nitro-hydrofluoric acid, however; and in fused hydrate and carbonate, but not in nitrate or chlorate of potassium.

II Graphitic silicon, made by charging metallic aluminium with silicon, by fusing it with silicofluoride of potassium, or powdered lead-free glass and cryolite. Aluminium &c., then dissolved away from cooled mass by hydrochloric and hydrofluoric acids. Hexagonal plates left, of sp. gr. 2·49, conductive of electricity. Graphitic silicon but slowly attacked by nitro-hydrofluoric acid, and by fused potash. Its peculiar reaction with dry hydrochloric acid gas, at a moderate heat, to form the compound HCl_3Si.

III Adamantine silicon, made by strongly heating aluminium in a current of chloride of silicon vapour, so as to sublime aluminic chloride and leave silicon in crystals. Lustrous, reddish-coloured, hexagonal prisms, hard enough to scratch glass:

$$3Cl_4Si + Al_4 = 2Cl_6Al_2 + Si_3$$

Or metallic zinc charged with silicon by its fusion with sodium and silicofluoride of sodium or potassium. After cooling, excess

of zinc melted out, and residue treated with acids, so as to leave silicon in form of long needles, composed of adhering octahedrons. Or the zinc volatilised off and fused silicon left, capable of being cast into bars. Or variously prepared silicon fused in crucibles of lime or charcoal, into steel-grey globules, lustrous like specular iron-ore, crystalline in structure, and composed of double hexagonal pyramids. Existence of adamantine and graphitic forms of silicon, as separate allotropic varieties of the element, doubtful.

(44.) Monad Siliconides.

Siliconetted hydrogen gas, H_4Si; made by dissolving in strong hydrochloric acid, the impure silicide of magnesium Mg_2Si, resulting from ignition of metallic sodium with mixed silicofluoride of sodium and chloride of magnesium:

$$Mg_2Si \quad + \quad 4HCl \quad = \quad H_4Si \quad + \quad 2Cl_2Mg$$

Siliconetted hydrogen also obtained by employing a positive pole of aluminium-silicon in the slow electrolysis of common salt solution.

A highly oxidisable gas, known only in admixture with hydrogen. Its spontaneous inflammability in air, or oxygen, with production of water and silica, or, in deficit of air, silicon. Its similar behaviour with chlorine. Its decomposition at a red heat. Its precipitation of silver- and copper-, but not of lead-solutions.

Fluoride of silicon, F_4Si; made by action of hydrofluoric acid on silica:

$$SiO_2 \quad + \quad 4HF \quad = \quad F_4Si \quad + \quad 2H_2O;$$

or, in practice, by action of sulphuric acid on mixture of fluor-spar with sand, or powdered flint, powdered glass, &c.:

$$SiO_2 \quad + \quad 2F_2Ca \quad + \quad 2H_2SO_4 \quad = \quad F_4Si \quad + \quad 2H_2O \quad + \quad 2Ca''SO_4$$

A liquefiable and solidifiable gas, of specific gravity $\frac{76+28}{2} = 52$.

Its combination with twice its volume of ammonia; and immediate decomposition by water or moisture.

Hydrosilicofluoric acid, H_2F_6Si; made by passing above gas through layer of mercury into water, and filtering off from precipitate of silicic acid:

$$4H_2O + F_4Si + 2F_4Si = H_4SiO_4 + 2(H_2F_2 . F_4Si)$$

Also by saturating dilute hydrofluoric acid with silica. Concentrated solution of acid, a sour fuming liquid, decomposible by evaporation into constituent fluorides of silicon and hydrogen, the latter attacking glass. Its neutralisation by alkalis to form moderately stable fusible salts, such as silicofluoride of potassium K_2F_6Si. Its precipitation of potassium and barium salts:

$$Cl_2Ba + H_2F_6Si = 2HCl + BaF_6Si$$

Chloride of silicon, Cl_4Si; made by heating silicon, or in practice an intimate mixture of silica and charcoal, in current of dry chlorine, and condensing product in cooled receiver:

$$C_2 + SiO_2 + Cl_4 = 2CO + Cl_4Si$$

Acrid, fuming liquid, boiling at 50°. Specific gravity of vapour $\frac{142 + 28}{2} = 85$. Its immediate decomposition by water, with exchange of chlorine for hydroxyl:

$$Cl_4Si + 4H_2O = (HO)_4Si \text{ or } H_4SiO_4 + 4HCl$$

Existence of similar bromide of silicon.

Chlorohydride of silicon, or silicon chloroform, HCl_3Si; made by passing dry hydrochloric acid gas over graphitic silicon, heated barely to redness, and condensing product. A mobile, fuming, inflammable liquid, boiling at 34°, and undergoing decomposition at a red heat. Its reaction with water to furnish silicon formic acid or leukone:

$$HCl_3Si + 2H_2O = H_2SiO_2 + 3HCl$$

Leukone, a snow-white powder, also produced by exposure to sun's rays of chryseone suspended in water. Chryseone, an orange yellow compound, made by action of hydrochloric acid on

silicide of calcium. Both leukone and chryseone unstable, reductive, inflammable bodies, decomposible by solutions of caustic alkali, and, at increased temperatures, by water alone, with evolution of hydrogen and formation of silicic acid or a silicate.

(45.) Silica and Silicates.

Relationship of orthosilicic acid H_4SiO_4 or $(HO)_4Si$, to silicic chloride Cl_4Si. Series of tetroxy-acids:

$HClO_4$	Perchloric
H_2SO_4	Sulphuric
H_3PO_4	Phosphoric
H_4SiO_4	Silicic

Orthosilicic acid not isolable, known in gelatinous and dissolved states, and represented by corresponding class of salts, as silicic ether Et_4SiO_4, olivine Mg_2SiO_4, zircon $ZrSiO_4$, &c.

Existence of metasilicic acid H_2SiO_3, or $H_4SiO_4-H_2O$, and of metasilicates. Also of other sets of compounds intermediate between the ortho-compounds and anhydride, or silica, SiO_2.

Crystalline silica met with in form of sand and quartz, the latter occurring either in crystalloïd masses, or distinct crystals, usually six-sided prisms with pyramidal summits. Finest form of crystalline quartz known as rock-crystal if colourless, amethyst if purple, rose-quartz if pink, and cairngorm if yellow or brown. Rock-crystal less hard than diamond or corundum. Its specific gravity 2·6. Its insolubility in solutions of alkali. Its unalterability by ignition, but capability of being pulverised after ignition and sudden quenching.

Native amorphous silica known as silex, exemplified by calcedony, carnelian, flint, &c. Transparent or semitransparent masses, having a stony rather than vitreous lustre. Specific gravity of silex variable, but below that of quartz. Its property of striking fire with steel. Its opacity after ignition. Change probably accompanied by some loss of water, organic matter, &c. Ignited flints easily reduced to opaque white powder. Solubility

of silex, especially after ignition, in solutions of caustic alkali. Opal closely related to calcedony. Presence in it of an appreciable quantity of water. Its specific gravity 2·1. Its hardness below that of silex, but its porosity and solubility greater. Presence of some crystalline silica in flint, calcedony, and opal.

Various forms of artificial amorphous silica. Its occurrence as washed and ignited precipitate formed by gradual acidification of solution of alkaline silicate; as gritty powder left on evaporating down hydrochloric acid solution or jelly of silica, and heating; as soft flocculi obtained by igniting precipitate formed by reaction of fluoride of silicon and water, &c. Artificial silica a white porous solid, absorbing moisture from the air, very mobile when heated, soluble in solution of caustic, and to some extent in that of carbonated alkali.

All varieties of silica, including rock-crystal, capable of being melted by oxihydrogen blowpipe into viscid transparent liquid, solidifying into glassy mass of specific gravity 2·2, attackable by solution of caustic alkali. Reaction of all varieties of silica with fused alkaline hydrate or carbonate, to form silicates, soluble in water and in excess of hydrochloric acid. Expulsion of carbonic anhydride from carbonates, and of other anhydrides from their respective salts, by silica at a sufficiently high temperature. Pure silica soluble in deficit of fused alkali-carbonate to form transparent colourless glass; and completely volatilisable when treated with hydrofluoric acid.

SILICIC ACIDS.

Aqueous solution made by adding alkaline silicate to excess of hydrochloric acid, and submitting liquid to dialysis for several days. Resulting 5 per cent. solution concentrated to 14 per cent. by ebullition in flask—not in open dish. Tasteless limpid liquid, having very faintly acid reaction, and gelatinising after some days. Gelatinisation retarded by presence of small amount of hydrochloric acid or caustic alkali; brought about almost immediately by addition of minute proportion of carbonic acid or a dissolved carbonate. Precipitability of aqueous silicic acid

by solutions of gelatin, alumina, and ferric oxide, with formation of silicates. Composition of residue left on evaporating aqueous acid to dryness in vacuo, H_2SiO_3.

Solution of silicic in hydrochloric acid best made by dissolving precipitated and washed silicate of copper in hydrochloric acid, and removing copper by sulphuretted hydrogen.

Occurrence of dissolved silica, probably as silicate, in most river- and spring-waters, containing carbonates. Increased solubility of silica in water heated under pressure, as that of Geyser springs.

Orthosilicic acid, H_4SiO_4 or $2H_2O.SiO_2$. Its probable existence in form of gelatinous precipitates thrown down by adding water to silicic fluoride and chloride; by neutralising hydrochloric acid solution of silicic acid; by acidifying solution of alkaline silicate; by decomposing zeolites with acid, &c. Ready solubility of precipitate in alkalis. Its sparing solubility in hydrochloric acid, save when in nascent state. Its dehydration by desiccation.

Parasilicic acid, $H_6Si_2O_7$ or $3H_2O.2SiO_2$, obtained as a glassy mass by action of moist air on silicic ether (Ebelmann). Metasilicic acid, H_2SiO_3 or $H_2O.SiO_2$, obtained by evaporation in vacuo of dialysed aqueous silica (Graham). Different anhydrosilicic acids, $2H_2O.3SiO_2$, $H_2O.3SiO_2$, &c., obtained by variously drying gelatinous silica (Doveri, Fuchs). Occurrence of natural hydrate of silica, above upper greensand formation, as a friable white deposit (Way).

Silicates; the most abundant class of natural minerals. Their existence in crystalline and massive states; both as distinct compounds, and as variously mixed constituents of heterogeneous rocks. Isomorphous mutual replacement in complex silicates of different metals or bases; more especially of magnesia and lime by one another, and by ferrous oxide; of lime by alkalis; of alkalis by one another; and of alumina by ferric oxide.

Ratio of oxygen of base to oxygen of silica as 2 to 2 in orthosilicates; most usually as 3 to 4, but variable between 2 to 2 and 1 to 2 in parasilicates; as 1 to 2 in metasilicates; and as 2 to 6

in anhydro-sesquisilicates. Existence also of other varieties of silicates.

Orthosilicates exemplified by olivine $Mg_2O_2.SiO_2$; and by the allied species garnet and idocrase $Ca_3Al_2O_6.Si_3O_6$.

Different varieties of parasilicates exemplified by common mica $Mg_4Al_2O_7.Si_4O_8$ (?), biaxial or potash mica $K_2Al_6O_{10}.Si_6O_{12}$, serpentine $Mg_3O_3.Si_2O_4.2Aq$, kaolin $Al_2O_3.Si_2O_4.2Aq$, chlorite $MgAl_2O_4(Mg_3O_3.Si_2O_4)3Aq$, and labradore $CaAl_2O_4.Si_3O_6$.

Metasilicates exemplified by allied species augite and hornblende $MgO.SiO_2$, and probably by talc $H_2Mg_5O_6.Si_6O_{12}$.

Anhydro-sesquisilicates exemplified by felspar or orthoclase $K_2Al_2O_4.Si_6O_{12}$, albite $Na_2Al_2O_4.Si_6O_{12}$, and meerschaum $Mg_2O_2.Si_3O_6.2$ & $4Aq$.

Granite and gneiss composed chiefly of quartz, felspar, and mica; syenite, of quartz, felspar and hornblende; porphyry and trachyte, of felspar; and basalt, of felspar with augite or labradore. Occurrence also of hornblende, intimately mixed with felspar or albite, in form of trap-rock; of chlorite, in different varieties of slate; and of serpentine, in serpentine-rock.

Native anhydrous silicates for the most part insoluble, fusible compounds, unattackable by mineral acids, save the hydrofluoric. Hydrated silicates, as serpentine, kaolin, &c., more or less readily attackable by acids. Certain hydrated alumino-silicates, especially of calcium, such for instance, as prehnite, stilbite, &c., classed as zeolites. Their property of boiling up before the blowpipe, and of dissolving readily in acids with separation of gelatinous hydrate of silica. All native silicates decomposible by excess of hydrofluoric acid, with complete volatilisation of silicon in form of fluoride. Their reaction with excess of fused alkali-carbonate to form alkali-silicates, readily decomposible by acids: *vide infra*.

Of artificial silicates, those of the alkali-metals alone soluble in water. Metasilicates of potassium and sodium $K_2O.SiO_2$, and $Na_2O.SiO_2$ usually made by fusing equivalent proportions of silica and alkali-carbonate:

$$Na_2CO_3 \text{ or } Na_2O.CO_2 \quad + \quad SiO_2 \quad = \quad Na_2SiO_3 \text{ or } Na_2O.SiO_2 \quad + \quad CO_2.$$

Deliquescent compounds, dissolving in water to form alkaline solution known as *liquor silicum*. Similar liquid made by boiling equivalent proportions of amorphous silica and strong solution of alkali-hydrate. Possibility of obtaining crystalline hydrated compounds, as $Na_2O.SiO_2.9Aq$, therefrom. Precipitation of hydrated silica from solution of alkali-silicate, by its gradual acidification, even with carbonic acid. Complete solubility of separated silica in excess of hydrochloric or other acid added suddenly, and its reprecipitation on subsequent neutralisation by alkali of resulting solution. Complete separation of silica by evaporating down acidified solution of alkali-silicate to dryness, and gently heating. Precipitation of other silicates as of silver, copper, &c., by action of *liquor silicum* on solutions of respective metals. Existence also of alkali-silicates referrible to class of ortho-compounds as $Na_4O_2.SiO_2$, and to class of para-silicates as $Na_6O_3.2SiO_2$.

Alkali-silicates with variable excess of silica, known as water-glass. Compounds made by fusing excess of silica, usually sand, with alkali-carbonate, and a little charcoal to facilitate reaction, &c. Proportions taken variable, ordinarily such as to yield compounds $K_2O.4SiO_2$ and $Na_2O.4SiO_2$. Resulting fused mass, having appearance of ordinary glass, powdered, and then boiled for some hours in water, until completely dissolved. Similar liquid made by digesting excess of amorphous silica, usually burnt flint, in strong solution of caustic alkali, heated under pressure. Both liquids further saturated, if necessary, by ebullition with freshly precipitated hydrate of silica, so as to form above tetrasilicates. Gelatinous precipitate of potash water-glass $K_2O.4SiO_2$, thrown down from its concentrated aqueous solution by addition of alcohol. Solution of water-glass perfectly neutral; of syrupy consistency when brought to sp. gr. of 1·25; and of firm gelatinous consistency when further evaporated. Decomposition of water-glass by all acids, including carbonic, with deposition of hydrated silica. Its conversion of lime, chalk, limestone, magnesian-limestone, &c. &c., into hard silicated masses. Use of water-glass in production of artificial stone, in

preservation of building stone, and in art of mural painting (stereochrome).

Use of intermediate alkali-silicates as ingredients of soap, and as dung-substitutes in dyeing, &c.

Glass, a variable mixture of silicate of alkali-metal and silicate of calcium or lead, with, in some cases, silicate of aluminum, &c. Its characteristic property of passing into a plastic state before fusion. Fusibility of glass below the mean fusibility of its constituent silicates. Principal varieties of glass known as crown or window-glass; plate-glass; crystal, flint- or white bottle-glass; and green bottle-glass. Window-glass a disilicate of calcium and sodium in about atomic proportions, represented approximatively by formula $(ca''Na)O.2SiO_2$. Plate-glass a trisilicate, with far less of lime than alkali, the latter often consisting in part of potash $(ca''Na)O.3SiO_2$. Bohemian hard glass a potash-lime trisilicate with at least as much lime as potash $(ca''K)O.3SiO_2$. Flint-glass chiefly a potash-lead trisilicate $(pb''K)O.3SiO_2$. Green bottle-glass an alumino-silicate of very variable composition, between $(ca''al'''Na)O.SiO_2$ and $2(ca''al'''Na)O.3SiO_2$. Partial replacement in it of alumina by ferric oxide, and of soda by potash. Solubility of different metallic oxides in molten glass, to produce coloured glass of various kinds. Enamel made by addition of comparatively infusible opaque substance, as peroxide of tin, to easily fusible glass.

Glass the type of a non-crystalline or vitreous body. Devitrefaction of glass, especially of green bottle-glass and water-glass, by slow cooling of fused mass. Unstable cohesion of suddenly solidified glass. Process of annealing. Expansibility of glass by, and its non-conductivity of heat. Indifference of ordinary well made glass to liquid chemical agents, other than hydrofluoric acid. But all glass, especially when in state of powder, or heated under pressure, more or less acted upon even by water. Absorption of carbonic acid from air, by moist powdered glass. Decomposition of inferior glass by dilute mineral acids. All glass more or less acted upon by solution of caustic alkali, in proportion to its concentration and temperature.

Existence of a silicic sulphide SiS_2, chlorosulphide Cl_2SiS, and nitride Si_2N_2 (?). Sulphide best made by igniting silicon in current of disulphide of carbon vapour. A white earthy substance, undergoing decomposition with, and complete solution in, water:

$$4H_2O + SiS_2 = 2H_2S + 2H_2O.SiO_2 \text{ or } H_4SiO_4$$

(46.) Carbon.

Its occurrence in uncombined state, as diamond, graphite, anthracite, &c.; combined with hydrogen, as marsh-gas, petroleum, &c.; with hydrogen and more or less oxygen, in coal and other inflammable minerals. Existence in the atmosphere of carbonic di-oxide or anhydride, evolved from earth-fissures, &c.; and in processes of respiration and combustion. The carbonates a very abundant class of minerals, exemplified by chalk and limestone, magnesian limestone, clay-iron-ore, &c. Occasional occurrence of mineral oxalates and mellitates. Peculiarity of carbon as the prime element of organic nature. Allotropic states and less distinct varieties of carbon. Specific heat of diamond 0·147, of natural graphite 0·202, of vegetable carbon 0·241 (Regnault). Query as to essential or accidental nature of above differences (Kopp). Atomic heat of carbon as diamond $0·147 \times 12 = 1·764$, instead of standard quantity 6·4. Same atomic heat, 1·8, of carbon in combination (Kopp).

Diamond. Its occurrence in form of small rounded transparent bodies, often having a thin opaque crust, in detritus of certain quartzose rocks of India, Borneo, Brazil, and the Urals. Its crystallisation in modified octahedral forms, with curved faces and edges. Specific gravity 3·5. Its non-conductivity of heat and electricity. Its extreme hardness, and employment for scratching and cutting glass. Its high lustre, transparency, refraction, dispersion, and occasional phosphorescence. Its capability of being heated somewhat strongly in air without change. But combustibility of ignited diamond in oxygen, with production of

carbanhydride, and separation of minute ash. Its unalterability by even an intense heat, under exclusion from air. Its conversion into a sort of graphite by heat of electric arc.

Graphite or plumbago met with in distinct beds, occurring in primitive rocks. Its existence in fine-grained or amorphous state, as that of Borrowdale, Passau, &c.; or in aggregation of crystalline scales, as that of Ceylon. Artificial production of crystalline graphite by solution of carbon in melted iron, and its extrusion therefrom on cooling. Its crystallisation in hexagonal plates belonging to rhombohedral system. Specific gravity 2·2. Its colour, opacity, semi-metallic lustre, and conductivity of heat and electricity. Its difficult combustibility in air, and more ready combustibility in oxygen gas, to form carbanhydride, and leave from 3 to 5 per cent. of ash. Its hardness and state of aggregation. Re-cohesion of powdered graphite under pressure. Its use in the manufacture of black-lead crucibles, lead pencils, as a lubricant, and to impart a non-oxidising and conductive surface.

Brodie's graphite compounds. Coarsely powdered graphite mixed with about 7 per cent. of potassium-chlorate, digested at a gentle heat in twice its weight of oil of vitriol (with or without some fluoride of sodium to expel silica), thoroughly washed with water, and dried. Product unaltered in appearance, but so changed as to undergo curious disintegration at red heat, with great increase in bulk, from interstitial evolution of gases.

Graphite mixed with three parts of potassium-chlorate, and digested in strong nitric acid at 60°, for several days, washed and dried. By several repetitions of process, original graphite changed into yellow silky plates of graphic acid, insoluble in water and acids, gelatinising with ammonia, and precipitable on acidifying ammonia-compound, as a white gelatinous mass. Composition of graphic acid represented by formula $H_4C_{11}O_5$. Effect of gradual heat on compound to leave residues with smaller and smaller proportions of oxygen, by its expulsion in forms of water, carbonous oxide, and carbanhydride. Effect of heat of 300° to decompose graphic acid explosively, leaving a bulky flocculent soot, still containing some hydrogen and oxygen. Re-

production of graphite from graphic acid, by action of reducing agents.

Anthracite, also known as blind or stone-coal, an amorphous, hard, lustrous, difficultly combustible, black solid, consisting of carbon to extent of 90 or 92 per cent. Its specific gravity 1·5 to 1·7. The so called graphites of New Brunswick and Greenland allied to anthracite. Typical varieties of coal exemplified by slightly bituminous Welsh or steam coal, intermediate Newcastle or caking coal, and highly bituminous Scotch or parrot coal. Bituminous shales, and solid bitumens.

Charcoal, or artificially produced carbon. Organic bodies in general regarded as imperfectly or un- oxidised compounds of carbon and hydrogen. Decomposition of hydrocarbons at a high temperature, with separation of carbon. Similar decomposition of oxihydrocarbons accompanied by burning away of more or less hydrogen in form of water.

Separation of carbon from various organic substances, by their imperfect combustion in deficit of air, a joint effect of removal of hydrogen by its preferential combustion, and of decomposition of substance by temperature resulting from the combustion.

Existence of carbon reduced from vapour, in forms of lamp-black, and of gas-carbon, or glance-coal.

Purest form of lamp-black made by passing vapour of ether, turpentine, &c., through red-hot porcelain tubes, and re-igniting deposit. Ordinary lamp-black, or soot, made by burning richly carbonaceous substances, such as tallow, resin, pitch, heavy tar-oil, &c., with limited supply of air. Thick black smoke conducted by flues into suitable chambers, lined with coarse cloth to receive deposit. Removal of soot by scraping cloth-walls, &c. Its subsequent calcination in iron vessels to destroy tarry matter. Presence of some hydrogen, however, even in re-ignited lamp-black. An amorphous, soft, dead-black powder, used chiefly in manufacture of printing ink. Its want of capillary affinity, as upon organic matter in solution, &c.

Gas-carbon, an extremely compact variety of charcoal, resulting from gradual decomposition of coal gas, by its contact

with strongly ignited roofs, &c., of the gas retorts; and producible in other ways. Its occurrence in pseudo-sublimed hard masses, of specific gravity 1·76, resembling both oven-coke and graphite in appearance, and of similarly difficult combustibility. Its almost metallic colour, lustre, sonorousness, and conductivity of heat and electricity.

Coke, cinder, or coal-charcoal. Object of manufacture to furnish fuel that does not cake in burning, or suffer local loss of heat by volatilisation from it of moisture, tar, &c. Presence of a variable amount of ash and other impurities in coke.

Oven-coke. Its production by submitting caking coal in quantities of several tons to a powerful heat, produced by its own partial combustion, for periods of 48 hours and upwards, in brick ovens with walls two or three feet thick to prevent cooling. Its columnar structure, steel-grey colour, semi-metallic lustre, excellent conductivity, great hardness, compact texture, and difficult combustibility.

Retort-coke, a residuary product in the manufacture of gas; made by heating a hundredweight or so of bituminous coal to a cherry-red heat for five or six hours, in close iron- or clay-retorts set in a furnace. Its dull black colour, porous texture, and comparatively easy combustibility. Compact or battery-coke made by strongly igniting a compressed mixture of coke and coal, saturating product with treacle, and re-igniting it.

Wood-charcoal or vegetable-carbon. Retention by wood-charcoal of exact form of original wood. Its considerable diminution in bulk, by 35 to 40 per cent.; and great diminution in weight, by 75 per cent. and upwards. Wood composed substantially of carbon, together with oxygen and hydrogen in proportion to form water. Volatilisation of water during ignition or combustion of wood, with consequent absorption of heat, and interference with attainment of local high temperature. Use of charcoal as a concentrated, flameless, radiating fuel, producing great local heat. Flaming fuel necessary to heat pottery-kilns, reverberatory furnaces, and large objects not in immediate proximity with fire-beds.

Rick- or pile-charcoal made by piling billets of dry wood into heaps, of ten or a dozen yards in diameter, afterwards covered with turf, and set fire to. Imperfect combustion of heaps continued for about a month. Product dense, and but slowly combustible.

Retort-charcoal made by distilling wood in comparatively small quantities at a time, for periods of four or five hours, in close iron retorts, heated to dull redness. A residuary product of the acetic acid manufacture. Also prepared specially from young dogwood, alder, &c., by gunpowder makers. Wood charred in current of steam, heated to 250° or 300°, known as *charbon roux*. Yield of charcoal proportionate to dryness, &c. of wood (Karsten), and to lowness of charring temperature (Violette). Percentage of carbon in charcoal proportionate to height of charring temperature. Presence of 1·0 to 1·5 per cent. of ash in ordinary wood-charcoal. Vegetable charcoal, free from ash, made by igniting pure crystallised sugar or well-washed starch. Tinder made by charring linen rags.

Animal-charcoal, bone- or ivory-black. Coarsely comminuted bones, freed from fat, ignited in iron retorts or pots. From 30 to 60 per cent. of original weight left, containing only 10 or 12 per cent. of carbon and about 90 per cent. of ash, removable to great extent by action of hydrochloric acid.

Different physical conditions of carbon or charcoal. Its conductivity of heat and electricity in proportion to its compactness. Its infusibility (?). Its fixity, contrasted with the volatility of its compounds. Absorption of gases and vapours by charcoal, more particularly by compact vegetable charcoal, as that of boxwood, cocoa-nut shell, &c. Absorption by boxwood charcoal of 90 volumes of ammonia, 55 of sulphuretted hydrogen, 35 of carbanhydride, and 9 of oxygen (Saussure). Absorption by cocoa-nut charcoal of 171 volumes of ammonia, 67 of carbanhydride, and 18 of oxygen (Hunter). Probable liquefaction of more absorbable gases in pores of the charcoal. Exalted chemical action of absorbed gases; whence catalytic (?) oxygenating and antiseptic properties of charcoal. Construction of charcoal ven-

tilating traps, respirators, &c. Absorption by charcoal of dissolved odorous, colouring, and other sparingly soluble matters, both mineral and organic. Decoloration of syrup in sugar refineries, by its filtration through animal charcoal. Washed residue of incinerated mixture of blood and carbonate of potassium still more efficient. Action of wood-charcoal in freeing water &c. from dissolved gases and essential oils.

Chemical inertness of charcoal at ordinary temperatures. Charring of stakes, casks, &c. Oxidisation of charcoal in moist way by sulphuric and nitric acids, &c. Its reduction of various metallic solutions. Its direct combinations with oxygen, sulphur, and hydrogen, at a red heat, to form carbanhydride CO_2, carbon disulphide CS_2, and klumene H_2C_2, respectively. Its combination with nitrogen in presence of alkali-metals, to form cyanides. Its combination with a few metals, as iron, to form carbides. Its reduction of steam at a red heat, and of metallic oxides and carbonates, &c.:

$$2H_2O + C = CO_2 + H_4$$
$$CO_2 + C = 2CO$$

Combustion of diamond, graphite, and charcoal in oxygen, alike productive of carbanhydride. Production of 44 parts by weight of carbanhydride for every 12 parts of carbon burnt:

$$C + O_2 = CO_2$$

Addition to weight, but not to bulk of oxygen, by its transformation into carbanhydride. Reproduction of carbon from carbanhydride by means of ignited potassium or sodium:

$$3CO_2 + Na_4 = 2Na_2CO_3 + C$$

Actual evolution of 96 units of heat by combination of 12 grammes of carbon with 32 grammes of oxygen. Absorption of much heat in virtual volatilisation of solid carbon into gaseous carbanhydride.

(47.) Monocarbon Compounds.

Principal mono-compounds of carbon with hydrogen, oxygen, and nitrogen:

H_4C	Marsh-gas or methene		
H_4CO	Wood-spirit or methyl alcohol		
H_2CO	Formic aldehyd		
H_2CO_2	Formic acid	CO	Carbonous oxide
H_2CO_3	Carbonic acid	CO_2	Carbanhydride
HCN	Prussic or hydrocyanic acid		
$HCNO$	Cyanic acid		

Existence of various sulpho- and chloro-derivatives, including chloroform Cl_3HC, phosgene Cl_2CO, sulphocyanic acid $HCNS$ &c.

Above tabulated compounds obtained from various sources. The simple oxides alone directly procurable from elementary carbon. Metamorphic relations of the different compounds with one another.

Methene H_4C, obtainable from methyl alcohol H_4CO, through intervention of methyl chloride, iodide, &c., by action thereupon of nascent hydrogen; from formic acid H_2CO_2, by its transmission over ignited baryta; and from disulphide of carbon CS_2, the sulpho-derivative of carbanhydride, by its joint reaction with sulphuretted hydrogen upon ignited metallic copper.

Methyl alcohol H_4CO, procurable from marsh-gas H_4C, by decomposition with potash of its chloro-derivative ClH_3C, resulting from exposure of mixed marsh-gas and chlorine to diffused daylight.

Formic aldehyd H_2CO; a recently discovered compound, obtainable from methyl alcohol by its aërial oxidation under influence of heated platinum wire.

Formic acid H_2CO_2, procurable from marsh-gas by decomposition of its derivative chloroform Cl_3HC with potash; from methyl alcohol H_4CO, and formic aldehyd H_2CO, by various oxidations; from carbonous oxide CO, by its indirect hydration with heated caustic potash; and from carbonic acid H_2CO_3, by its deoxidation with metallic sodium. Carbonous oxide CO, formed by dehydration of formic acid H_2CO_2, with oil of vitriol, &c.; and by deoxidation of carbanhydride CO_2, with ignited iron, carbon, hydrogen, &c.

Carbonic acid H_2CO_3, procurable from marsh-gas H_4C,

methyl alcohol H_4CO, formic aldehyd and acid, H_2CO and H_2CO_2, by various oxidations, as with moist chlorine for instance; from carbanhydride CO_2, by indirect hydration with caustic potash, &c.; and from carbonous oxide CO, through intervention of phosgene Cl_2CO, by its decomposition with water. Carbanhydride CO_2, producible by mere desiccation of carbonic acid H_2CO_3, and direct oxidation of carbonous oxide CO.

Relationship of formic acid H_2CO_2, and carbonous oxide CO, to hydrocyanic acid HCN. Absorption by latter acid of one atom of water when heated with oil of vitriol, and of two atoms of water when heated with potash:

$$HCN + H_2O = H_3N + CO$$
$$HCN + 2H_2O = H_3N + H_2CO_2$$

Similar relation of carbonic acid and anhydride to cyanic acid HCNO:

$$HCNO + H_2O = H_3N + CO_2$$
$$HCNO + 2H_2O = H_3N + H_2CO_3$$

Actual appearance of resulting formic and carbonic acids as potassium salts; and of ammonia, in oil of vitriol reactions, as sulphate.

Monocarbon compounds divisible into three groups, namely, the methylic typified by marsh-gas H_4C; the formic typified by formic aldehyd or oxi-marsh-gas H_2CO''; and the cyanic typified by hydrocyanic acid or nitro-marsh-gas HCN'''. Derivation of cyanic compounds (*vide* § 55).

(48.) METHENE.

Marsh-gas or methyl hydride H_4C. Its natural occurrence as marsh-gas, fire-damp, inflammable air, &c. Its existence also as the chief constituent of coal-gas, and as a product of the destructive distillation of organic matter in general.

a. Its formation, by decomposition of acetic acid at a red heat. In practice, mixture of sodium acetate, caustic soda, and lime heated in coated flask:

$$NaH_3C_2O_2 + NaHO = H_4C + Na_2CO_3$$

β. Its formation from its derivatives, methyl chloride ClH_3C, chloroform Cl_3HC, &c., by means of nascent hydrogen:

$$Cl_3HC \quad + \quad H_6 \quad = \quad H_4C \quad + \quad 3HCl$$

Also, from moist methyl iodide, by action of zinc; or from equivalent decomposition of zinc methide by water, mercuric methide by hydrochloric acid, &c.:

$$Zn_2 \quad + \quad 2IH_3C \quad + \quad H_2O \quad = \quad 2H_4C \quad + \quad \overbrace{ZnO \quad + \quad ZnI_2}$$

$$Zn''(H_3C)_2 \quad + \quad H_2O \quad = \quad 2H_4C \quad + \quad ZnO$$

γ. Its production in small quantity, by transmission of mixed disulphide of carbon vapour and sulphuretted hydrogen over ignited copper:

$$CS_2 \quad + \quad 2H_2S \quad + \quad Cu_8 \quad = \quad H_4C \quad + \quad 4Cu_2S$$

Also, from decomposition of formic acid, or rather formiate of barium, at a red heat:

$$2Ba\begin{cases}HCO_2\\HCO_2\end{cases} \quad = \quad 2BaCO_3 \quad + \quad CO_2 \quad + \quad H_4C$$

A neutral, insoluble, incondensable gas, of specific gravity $\frac{4+12}{2} = 8$, rather more than half that of atmospheric air. Its gradual decomposition at a white heat, or by means of electric sparks, into carbon and hydrogen (with a small quantity of acetylene), the original two volumes becoming nearly four. Its inflammability in or with air. Results of its explosion with air or oxygen:

$$H_4C \quad + \quad O_4 \quad = \quad CO_2 \quad + \quad 2H_2O$$

$$H_4C \quad + \quad O_2 \quad = \quad CO \quad + \quad H_2O \quad + \quad H_2$$

Explosions of fire-damp and air in mines, and of coal-gas and air in houses, &c. High temperature necessary for combustion of marsh-gas, and of hydrocarbonous substances in general. Extinction of flame by cooling action of metal gauze, &c. Principle of Davy's safety lamp, of Hemming's safety jet, &c.

Gradual reaction of marsh-gas with excess of moist chlorine to form hydrochloric acid, and carbonic acid or anhydride:

$$2H_2O \quad + \quad H_4C \quad + \quad Cl_8 \quad = \quad CO_2 \quad + \quad 8HCl$$

Results of its combustion in, or explosion with chlorine:

$$H_4C \quad + \quad Cl_4 \quad = \quad C \quad + \quad 4HCl$$

Effect of sunlight in producing explosion of mixed marsh-gas and chlorine, especially with the latter in excess. Gradual reaction of equal volumes of dry marsh-gas and chlorine, exposed to diffused daylight:

$$H_4C \quad + \quad Cl_2 \quad = \quad ClH_3C \quad + \quad HCl$$

Production of chloroform and other chloro-derivatives, by action of excess of chlorine on marsh-gas, diluted with carbanhydride to prevent explosion:

$$H_4C \quad + \quad Cl_6 \quad = \quad Cl_3HC \quad + \quad 3HCl$$

Corresponding action of chlorine upon marsh-gas H_4C, and hydrogen H_2, viewed as hydride of methyl and hydride of hydrogen respectively:

$$\begin{array}{lclclcl} HH & + & Cl_2 & = & HCl & + & ClH \\ H(H_3C) & + & Cl_2 & = & HCl & + & Cl(H_3C) \end{array}$$

Hydrogen and marsh-gas procurable by similar decompositions of formic acid H_2CO_2, and acetic acid $H_4C_2O_2$, respectively:

$$\begin{array}{lclcl} H_2CO_2 & = & H_2 & + & CO_2 \\ H_4C_2O_2 & = & H_4C & + & CO_2 \end{array}$$

(49.) Methyl Alcohol.

Methyl hydrate, or wood-spirit, H_4CO, or $H(H_3C)O$, or $(HO)H_3C$; a derivative of marsh-gas by substitution of (HO) for H, and of water by substitution of (H_3C) for H. Its reactions mostly expressible as exchanges of water residue (HO) for chlorous radical as H or Cl, &c.; or, what comes to the same thing, as exchanges of marsh-gas residue (H_3C) for basylous radical, as H or K, &c.

Relationship of marsh-gas and methyl chloride respectively to wood-spirit or methyl alcohol, that of hydrogen and hydrochloric acid to water:

H_2	ClH	$(HO)H$	HHO
H_4C	ClH_3C	$(HO)H_3C$	$H(H_3C)O$

a. Methyl alcohol produced from marsh-gas, through intervention of methyl chloride, by its double decomposition with potash:

$$Cl(H_3C) \;+\; HKO \;=\; ClK \;+\; H(H_3C)O$$
$$\text{or } (HO)K \;+\; Cl.H_3C \;=\; ClK \;+\; (HO)H_3C$$

β. Methyl alcohol obtainable in pure state by decomposing with alkali, not only above methyl chloride, but also native methyl salicate (*Gaultheria oil*), and artificial methyl oxalate, citrate, benzoate, &c.:

$$H_5(H_3C)C_7O_3 \;+\; HNaO \;=\; NaH_5C_7O_3 \;+\; H(H_3C)O$$

γ. Methyl alcohol usually procured, in first instance, from brown watery liquid obtained in pyroligneous acid factories, by destructive distillation of wood. Most volatile portion of liquid distilled off, treated with slaked lime, and redistilled. Methyl-alcohol of resulting crude wood-spirit fixed by its combination with chloride of calcium, and volatile impurities expelled by heat of water-bath. Chloride of calcium compound then decomposed by water, and its methyl alcohol distilled off. Further purification of the alcohol by its filtration in diluted state through wood-charcoal, and rectification, finally off quicklime. Or, if necessary, by its conversion into methyl oxalate, &c., decomposible as above.

Methyl alcohol, a spirituous liquid, fragrant when pure, empyreumatic and nauseous when crude. Sp. gr. 0·814 at 0°. Boiling point 61°. Vapour-density, $\frac{4+12+16}{2}=16$. Its general resemblance to spirit of wine. Its compounds with baryta and chloride of calcium, $BaO.2H_4CO$, and $Cl_2Ca.4H_4CO$, respectively. Solubility of caustic soda in wood-spirit, with double

decomposition (?). Reaction of wood-spirit with metallic sodium, to form sodium methylate:

$$2H_4CO \quad + \quad Na_2 \quad = \quad 2NaH_3CO \quad + \quad H_2$$

Its direct oxidation into formic aldehyd and acid by various processes, including exposure to air in presence of platinum:

$$H_4CO \quad + \quad O \quad = \quad H_2CO \quad + \quad H_2O$$
$$H_4CO \quad + \quad O_2 \quad = \quad H_2CO_2 \quad + \quad H_2O$$

Its reaction with heated soda-lime, to produce sodium-formiate:

$$H_4CO \quad + \quad NaHO \quad = \quad NaHCO_2 \quad + \quad H_4$$

Its reaction with chlorine, to produce indefinite compounds; with hypochlorites, to produce chloroform:

$$4H_4CO \quad + \quad 8NaClO \quad = \quad Cl_3HC \quad + \quad 3NaHCO_2 \quad + \quad 6H_2O \quad + \quad 5NaCl$$

Its reaction with chloride of hydrogen, and electro-negative chlorides, to form methyl chloride:

$$Cl_5P \quad + \quad H(H_3C)O \quad = \quad Cl_3PO \quad + \quad ClH \quad + \quad ClH_3C$$

Its reaction with sulphate of hydrogen or sulphuric acid, to form the two methyl sulphates (*vide infra*); and with excess of heated sulphuric acid to form methyl oxide or so-called simple methyl-ether:

$$H_2SO_4 \quad + \quad \overbrace{H(H_3C)O \quad + \quad H(H_3C)O} \quad = \quad \overbrace{H_2SO_4 \quad + \quad H_2O} \quad + \quad (H_3C)_2O.$$

METHYL SALTS.

Saline methyl-ethers, or methyl-salts, derivable from various acids by replacement of their basic hydrogen by methyl. Typical production of compound ethers from alcohol and acid with elimination of water, and their transformation into alcohol and acid with absorption of water:

$$HCl \quad + \quad H(H_3C)O \quad = \quad H_3C.Cl \quad + \quad H_2O$$

Replacement in polybasic acids of some or all of their

basic hydrogen by methyl, to form acid or neutral methyl-ethers:

$$H_2SO_4 + H(H_3C)O = H(H_3C)SO_4 + H_2O$$
$$H_2SO_4 + 2H(H_3C)O = (H_3C)_2SO_4 + 2H_2O$$

Virtual neutralisation of acids by methyl alcohol or hydrate, as by sodium hydrate, &c.

α. Saline ethers usually made by acting upon the alcohol, or in some cases its simple ether or oxide, with the acid, or its anhydride, or chloride. (*Vide supra.*)

β. By double decomposition of some pre-formed saline ether with a salt of the acid, or in a few cases with the acid itself, of which the ether is required. (*Vide infra.*)

γ. By adding strong sulphuric acid to, or passing current of hydrochloric acid gas through, mixture of the alcohol with salt of the acid, or in some cases with the acid itself, of which the ether is required. (*Vide* methyl-halides.)

The majority of neutral methyl-ethers spirituous or oily liquids, insoluble in water, soluble in alcohol and ether, volatile without decomposition and characteristically odorous. But the oxalate $(H_3C)_2C_2O_4$, the citrate $(H_3C)_3H_5C_6O_7$, and a few others, solid and crystalline.

Action of chlorine upon saline ethers to form chloro-derivatives, with 2, 4, and 6, &c., atoms of hydrogen replaced by chlorine; as upon formic methyl-ether $(H_3C)HCO_2$ or $H_4C_2O_2$, oxalic methyl-ether $(H_3C)_2C_2O_4$ or $H_6C_4O_4$, &c.:

$$H_4C_2O_2 \qquad Cl_2H_2C_2O_2 \qquad Cl_4C_2O_2$$
$$H_6C_4O_4 \qquad Cl_2H_4C_4O_4 \qquad Cl_4H_2C_4O_4 \qquad Cl_6C_4O_4$$

Reaction of saline neutral ethers with alkali, and occasionally with water, to reproduce original acid or its salt, and original alcohol, together in some cases with its simple ether:

$$(H_3C)HCO_2 + KHO = KHCO_2 + H(H_3C)O$$
$$(H_3C)_2C_2O_4 + 2H_2O = H_2C_2O_4 + 2H(H_3C)O$$

Intermediate reaction of some polymethylic neutral ethers with water, to form acid ethers, as methyl-sulphuric acid:

$$(H_3C)_2SO_4 + H_2O = H(H_3C)SO_4 + H(H_3C)O$$

Reaction with ammonia of some methyl-ethers, as the nitrate, chloride, &c., to form methylamine salts (*vide* methylamines):

$$\left.\begin{matrix}H_3C\\NO_2\end{matrix}\right\}O \quad \text{or} \quad (H_3C)NO_3 \quad + \quad H_3N \quad = \quad HNO_3.H_2(H_3C)N$$

Reaction with ammonia of most methyl-ethers, to form amides of the etherified acids, as formiamide, oxamide, &c.:

$$\left.\begin{matrix}H_3C\\HCO\end{matrix}\right\}O \text{ or } (H_3C.O)HCO \; + \; H_3N \;=\; H_2N.HCO \; + \; H(H_3C)O$$

$$\left.\begin{matrix}(H_3C)_2\\C_2O_2\end{matrix}\right\}O_2 \text{ ,, } (H_3C.O)_2C_2O_2 \; + \; 2H_3N \;=\; (H_2N)_2C_2O_2 \; + \; 2H(H_3C)O$$

Intermediate reaction of some polymethylic ethers with ammonia, to form ether-amides, as sulphamethylane:

$$\left.\begin{matrix}(H_3C)_2\\SO_2\end{matrix}\right\}O_2 \text{ or } (H_3C.O)_2SO_2 \; + \; H_3N \;=\; H_3C.O(H_2N)SO_2 \; + \; H(H_3C)O$$

The majority of acid methyl-ethers, unstable compounds, rarely volatile without decomposition, mostly soluble in, and easily decomposible by, water. The methyl-sulphates of potassium and barium $K(H_3C)SO_4$, and $Ba''(H_3C.SO_4)_2$, much used for furnishing other ethers by double decomposition. Reaction of potassium methyl-sulphate with potassium cyanide, for instance (*vide supra* β):

$$K(H_3C)SO_4 \quad + \quad KCN \quad = \quad K_2SO_4 \quad + \quad (H_3C)CN$$

VARIOUS METHYL DERIVATIVES.

Relationship of methyl-alcohol to methyl-chloride and methylamine, parallel with that of water to hydrochloric acid and ammonia. The three methylic bodies regarded as derivatives of hydrochloric acid, water, and ammonia, respectively, by subsitution of one atom of methyl for one atom of hydrogen:

HCl	$(H_3C)Cl$	ClH	$(Cl)H_3C$
H_2O	$H(H_3C)O$	$(HO)H$	$(HO)H_3C$
H_3N	$H_2(H_3C)N$	$(H_2N)H$	$(H_2N)H_3C$

Further substitution of methyl for hydrogen in water, to produce methyl-oxide or ether $(H_3C)_2O$; and in ammonia, to produce di- and tri- methyl-amines, $H(H_3C)_2N$ and $(H_3C)_3N$ respectively.

Substitution of methyl for hydrogen in marsh-gas H_4C, to produce methyl-methyl $H_3C.H_3C$, or ethene H_6C_2, or hydride of ethyl $H.H_5C_2$. Ordinary alcohol H_6C_2O, the corresponding hydrate $H(H_5C_2)O$; ether the corresponding oxide $(H_5C_2)_2O$; ethylamine the corresponding amide $H_2(H_5C_2)N$, &c. &c. General similarity of methyl- and ethyl- compounds. Homologous series of fatty hydrocarbons and alcohols, &c., and of acids resulting from oxidation of alcohols:

Hydrocarbon		Alcohol, &c.		Acid	
H_2	Hydrogen	H_2O	Water		
$H_4\,C$	Marsh-gas	$H_4\,C\,O$	Methyl-	$H_2\,C\,O_2$	Formic
$H_6\,C_2$	Ethene	$H_6\,C_2O$	Ethyl-	$H_4\,C_2O_2$	Acetic
$H_8\,C_3$	Propene	$H_8\,C_3O$	Propyl-	$H_6\,C_3O_2$	Propion
$H_{10}C_4$	Butene	$H_{10}C_4O$	Butyl-	$H_8\,C_4O_2$	Butyric
$H_{12}C_5$	Eupione	$H_{12}C_5O$	Amyl-	$H_{10}C_5O_2$	Valeric
$H_{14}C_6$	Caprene	$H_{14}C_6O$	Capryl-	$H_{12}C_6O_2$	Caproic

Substitution of methyl for hydrogen in pyrogenous hydrocarbon phenene H_6C_6, to form benzoene $H_3C.H_5C_6$, or H_8C_7, or $H.H_7C_7$. Benzyl-alcohol $H(H_7C_7)O$, the corresponding hydrate, benzyl-amine $H_2(H_7C_7)N$, the corresponding amide, &c. Homologous series of aromatic hydrocarbons and alcohols, &c., and of acids resulting from oxidation of alcohols:

$H_6\,C_6$	Phenene	$H_6\,C_6O$	Phenyl-		
$H_8\,C_7$	Benzoene	$H_8\,C_7O$	Benzyl-	$H_6C_7O_2$	Benzoic
$H_{10}C_8$	Xylene	$H_{10}C_8O$	Xylyl-?	$H_8C_8O_2$	Toluic

METHYL HALIDES, ETC.

Marsh-gas compounds in which one or more atoms of hydrogen are substituted by a monad element.

Methyl fluoride, FH_3C; a gas, similar in its properties to methyl chloride, made by heating mixture of wood-spirit and sulphuric acid with fluoride of potassium. (*Vide* methyl salts, γ.)

Methyl chloride or chloromethene, $Cl.H_3C$; produced by reaction of chlorine upon marsh-gas (*vide supra*), or of electro-negative chlorides, as of phosphorus, hydrogen, &c., upon methyl hydrate. Usually made by distilling mixture of wood-spirit and sulphuric acid with common salt (*vide* methyl-salts, γ):

$$ClNa + H_2SO_4 + H(H_3C)O = ClH_3C + NaHSO_4 + H_2O$$

A difficultly condensable, soluble, inflammable gas, of ethereal taste and odour. Its decomposition at a red heat, with evolution of hydrochloric acid. Its reaction with potash or water to form methyl-hydrate, with ammonia to form methyl-amine, with nascent hydrogen to form marsh-gas, and with chlorine to form higher chloro-derivatives.

Methylen chloride or dichloromethene, Cl_2H_2C; the most volatile product of the action of chlorine upon methyl chloride. Also producible by action of nascent hydrogen upon chloroform; and in other ways. A mobile liquid boiling at 30·5°, scarcely decomposible by distillation off caustic potash.

Chloroform or trichloromethene, Cl_3HC; formed, together with chloride of carbon, by action of chlorine on marsh-gas and its lower chloro-derivatives. Also from trichloraldehyd or chloral by ebullition with, and from trichloracetic acid by dry distillation with, caustic alkali:

$$Cl_3HC_2O + KHO = Cl_3HC + KHCO_2$$
$$Cl_3KC_2O_2 + KHO = Cl_3HC + K_2CO_3$$

Chloroform usually made by distilling spirit of wine or wood-spirit with bleaching powder, excess of slaked lime, and water. Production from two atoms of alcohol $2H_6C_2O$, or from four atoms of wood-spirit $4H_4CO$, of one atom of chloroform, and of three atoms of either formiate or carbonate of alkali-metal, according to extent of oxidation. Reaction with sodium hypochlorite:

$$2H_6C_2O + 8NaClO = Cl_3HC + 3NaHCO_2 + 4H_2O + 5NaCl$$

A thin, oily liquid, of sp. gr. 1·48, and boiling point 61°, of ethereal fruity odour, inflammable from a wick though not very

readily, immiscible with water, freely soluble in alcohol and ether, and a solvent for fats, resins, caoutchouc, most organic alkaloids, phosphorus, sulphur, and iodine—a mere trace of iodine sufficing to give to it a bright crimson colour. Its gradual decomposition by strong sulphuric acid, with liberation of hydrochloric acid. Its reaction with alcoholic solution of caustic potash to produce potassium chloride and formiate:

$$Cl_3HC + 4KHO = 3KCl + KHCO_2 + 2H_2O;$$

Its reaction with ammonia, especially in presence of potash, to form hydrocyanic acid or a cyanide:

$$Cl_3HC + H_3N = 3HCl + HCN;$$

Its reaction with chlorine to produce perchloride of carbon; and with nascent hydrogen to produce lower chloro-derivatives, and finally marsh-gas. Its decomposition at a red heat, with production of hydrochloric acid and chlorine.

Perchloride of carbon or tetra-chloromethene, Cl_4C; made, together with chloroform, by exposing to sunlight mixture of chlorine in excess, and marsh-gas, diluted with carbanhydride to prevent explosion; or by passing current of dry chlorine through chloroform at a boiling heat:

$$Cl_3HC + Cl_2 = Cl_4C + HCl$$

Also commercially from disulphide of carbon, by its reaction with chlorine; either at a red heat, or, in presence of sulphur, iodine, or chloride of antimony, at a boiling heat:

$$CS_2 + Cl_6 = Cl_4C + Cl_2S_2$$

Resulting perchloride of carbon separated from chloride of sulphur by distillation off caustic alkali.

An oily liquid, very similar to chloroform, of sp. gr. 1·56 and boiling point 77°. Its reaction with nascent hydrogen, evolved by sodium amalgam, to yield in succession Cl_3HC, Cl_2H_2C, ClH_3C, and H_4C. Its reaction with sulphuretted hydrogen to yield the sulphochloride Cl_2CS, and hydrochloric acid. Its slow reaction with alcoholic potash to yield chloride, and carbonate

instead of formiate of potassium. Its decomposition at a red heat into chlorine and sesquichloride of carbon, the latter decomposing partially into chlorine and perchlorethylene:

$$2Cl_4C = Cl_6C_2 + Cl_2$$
$$Cl_6C_2 = Cl_4C_2 + Cl_2$$

Methyl bromide, BrH_3C; made by cautious action of phosphorus and bromine on wood-spirit. Formation and properties of compound similar to those of chloride and iodide. An ethereal liquid of sp. gr. 1·66, and boiling point 13°.

Methyl iodide, IH_3C. An important reagent, made by acting with phosphorus and iodine upon wood-spirit. Reaction similar to that of same bodies on water, yielding iodide of hydrogen or hydriodic acid:

$$3H(H_3C)O + I_3P''' = H_3P'''O_3 + 3IH_3C$$

A colourless liquid, of sp. gr. 2·2, boiling point 43°, almost insoluble in water, not readily inflammable. Its reaction with potassium hydrate or potash to re-form hydrate of methyl; and with potassium ethylate to form ethylate of methyl:

$$I.H_3C + HKO = IK + H(H_3C)O$$
$$I.H_3C + H_5C_2KO = IK + H_5C_2(H_3C)O$$

Its reaction with ammonia and many organic alkaloids, to form hydriodides of the methyl-amines and of other methyl-alkaloids:

$$I.H_3C + H_3N = IH.H_2(CH_3)N$$

Its direct combination, under suitable conditions, with zinc, mercury, &c., to form metallic iodo-methides, as $I(H_3C)Zn''$, and $I(H_3C)Hg''$. Its reaction with sodium-alloys, as sodium antimonide, to form iodide of sodium and methide of other metal, as methyl-stibine.

Iodoform or trisiodomethene, I_3HC; produced by action of a hypiodite, or mixture of iodine with caustic or carbonated alkali, upon alcohol, wood-spirit, gum, albumin, and divers organic substances. Also by action of hypochlorites upon an alcoholic solution of potassium iodide. Usually made by adding

alcohol, and then iodine, little by little, to a warm solution of sodium carbonate:

$$2H_6C_2O + 8NaIO = I_3HC + 3NaHCO_3 + 4H_2O + 5NaI$$

After separation of precipitated iodoform, additional deposit obtained by passing slow current of chlorine through mother liquor, to utilise iodine of resultant iodide of sodium. Occurrence of iodoform in yellow, fusible, hexagonal plates of sp. gr. 2·0, melting at 115° to 120°, volatilising in vapour of water, but undergoing partial decomposition when heated alone, insoluble in water, soluble in ether, alcohol, fixed and essential oils, &c. Its reactions similar to those of chloroform. Chloriodoform Cl_2IHC, produced by its distillation with corrosive sublimate; and cyaniodoform $(CN)I_2HC$ by treating its alcoholic solution with cyanogen.

Chloropicrin, $Cl_3(NO_2)C$; a product of the complex decomposition of nitro-picric acid by bleaching powder; and Marignac's oil $Cl_2(NO_2)_2C$, a product of the action of nitric acid upon chloride of naphthalene. Reaction of chloropicrin with nascent hydrogen and with ammonia, to form hydrochlorides of methylamine and of guanidine respectively.

METHYL OXIDES, ETC.

Methyl hydrate or -alcohol, H_4CO or $H(H_3C)O$, preconsidered. (*Vide par.* 49.)

Methyl oxide or -ether, H_6C_2O or $(H_3C)_2O$; a gaseous body, formed under various circumstances by dehydration of methyl alcohol:

$$2H(H_3C)O = (H_3C)_2O + H_2O$$

Its usual production by heating one part of methyl alcohol with four parts of oil of vitriol. Gas purified by potash, and collected over mercurial trough. Its specific gravity, $\frac{6+24+16}{2} = 23$. Reaction effected at two stages. Final result a dehydration of the alcohol, as above:

$$H_2SO_4 + H(H_3C)O = \mathit{H(H_3C)SO_4} + H_2O$$
$$\mathit{H(H_3C)SO_4} + H(H_3C)O = H_2SO_4 + (H_3C)_2O$$

Isomerism of methyl-ether with alcohol. Its ethereal odour, inflammability, considerable solubility in water, great solubility in alcohol and ether, and condensability by intense cold. Its absorption by sulphuric anhydride to form neutral methyl sulphate:

$$(H_3C)_2O \quad + \quad SO_3 \quad = \quad (H_3C)_2SO_4$$

Its spontaneous explosion with chlorine. Its reaction by cautious admixture with chlorine to form series of derivatives, $Cl_2H_4C_2O$, $Cl_4H_2C_2O$, and Cl_6C_2O.

Methyl sulphydrate, or -mercaptan, H_4CS or $H(H_3C)S$; made by distilling together strong solutions of sulphydrate and methyl-sulphate of potassium (*vide* methyl-salts, β):

$$K(H_3C)SO_4 \quad + \quad HKS \quad = \quad K_2SO_4 \quad + \quad H(H_3C)S$$

A colourless liquid, lighter than and insoluble in water, boiling at 21°, and having a most offensive odour. Its reaction with mercuric oxide to form mercuric methyl-mercaptan $Hg''(H_3C.S)_2$, as a white crystallisable compound.

Methyl sulphide, H_6C_2S or $(H_3C)_2S$; made by saturating wood-spirit solution of sulphide of potassium with chloride of methyl gas and distilling (*vide* methyl-salts, β):

$$2Cl(H_3C) \quad + \quad K_2S \quad = \quad 2ClK \quad + \quad (H_3C)_2S$$

A colourless, insoluble, extremely offensive liquid, of sp. gr. 0·845 and boiling point 41°. Its reaction with chlorine to form series of derivatives $Cl_2H_4C_2S$, $Cl_4H_2C_2S$, and Cl_6C_2S, corresponding to those of the oxide.

Methyl disulphide, $(H_3C)_2S_2$; produced as a perfectly definite compound, boiling at 116°, by substituting disulphide, for sulphydrate or sulphide of potassium, in above two reactions. Sulphydrate and two sulphides of methyl oxidisable by nitric acid into methyl-sulphurous acid $H(H_3C)SO_3$. Methyl selenide $(H_3C)_2Se$, similarly producible from potassium selenide, analogous in character to the sulphide, oxidisable by nitric acid into methyl-selenious acid $H(H_3C)SeO_3$. Methyl telluride $(H_3C)_2Te$, produced similarly from potassium telluride. (*Vide* metal-methides.)

METHYL-AMINES.

Relation of three methylamines to ammonia, similar to that of methyl alcohol and -ether to water, and to that of methyl-chloride to hydrochloric acid:

HCl	H_2O	H_3N	H_3N
$(H_3C)Cl$	$H(H_3C)O$	$H_2(H_3C)N$	H_5CN
	$(H_3C)_2O$	$H(H_3C)_2N$	H_7C_2N
		$(H_3C)_3N$	H_9C_3N

Their occurrence as volatile alkaline substances, manifesting a general resemblance to ammonia, and having the characteristic property of forming salts by their direct union with different acids, as with the hydrochloric and hydriodic acids, for instance:

$ClH.H_2(H_3C)N$	Hydrochloride of methylamine
$IH.H(H_3C)_2N$	Hydriodide of di-methylamine

Decomposition of salts of mono- di- and tri-methylamine by fixed alkalis and basic oxides, with reproduction of respective methylamines:

$$IH.(H_3C)_3N \quad + \quad KHO \quad = \quad KI \quad + \quad (H_3C)_3N \quad + \quad H_2O$$

Further property of trimethylamine to unite with the chloride, iodide, &c., not only of hydrogen but of methyl, ethyl, &c., to form, for instance, methyl-iodide of trimethylamine or iodide of tetramethylium:

$$I.H_3C \quad + \quad (H_3C)_3N \quad = \quad I.H_3C(H_3C)_3N \quad \text{or} \quad I(H_3C)_4N$$

Iodide of tetramethylium undecomposible by hydrate of potassium; but transformable into hydrate of tetramethylium by its reaction with moist hydrate of silver:

$$I(H_3C)_4N \quad + \quad AgHO \quad = \quad AgI \quad + \quad HO.(H_3C)_4N$$

Hydrate obtainable in dry state, as a caustic deliquescent solid; volatilisable only with decomposition.

Reaction of di- and mono-methylamines with iodide of methyl to form hydriodides of higher methylamines, as $IH(H_3C)_3N$ obtainable from $I(H_3C)$ and $H(H_3C)_2N$.

Reaction of alcoholic solution of ammonia with iodide of methyl, heated under pressure, to form all five iodides:

$IH.H_3N$; $IH.H_2(H_3C)N$; $IH.H(H_3C)_2N$; $IH.(H_3C)_3N$; $I(H_3C)_4N$.

First and last compounds formed in largest proportion. Last compound easily separated through its sparing solubility. Solution of other products evaporated down, the residue distilled with potash, and distillate passed through freezing mixture. Trimethylamine and dimethylamine, with some dissolved methylamine, condensed as liquid, remainder of methylamine together with ammonia, passing on as gas, absorbable by water or dilute acid.

Methylamine, H_5CN or $H_2(H_3C)N$. Its occurrence among products of destructive distillation and putrefaction of animal matter. Its formation also by decomposition, under various circumstances, of many animal and vegetable alkaloids.

α. Its production, as above described, by reaction of methyl iodide with ammonia; and decomposition of resulting hydriodide by potash:

$$I.H_3C \quad + \quad H_3N \quad = \quad IH.H_2(H_3C)N$$

Methylamine separated from ammonia by distinctive solution of its salts in absolute alcohol; separated from di- and tri-methylamine by its reaction with oxalic ether to form dimethyl-oxamide, a compound insoluble in cold water, but capable of being crystallised from boiling water. Pure methylamine liberated by decomposition of dimethyl-oxamide with potash.

β. Production of methylamine, by decomposition with potash of cyanate and cyanurate of methyl, similar to production of ammonia by decomposition of cyanate of hydrogen:

$$2KHO \quad + \quad HCNO \quad = \quad K_2CO_3 \quad + \quad H_3N$$
$$2KHO \quad + \quad (H_3C)CNO \quad = \quad K_2CO_3 \quad + \quad H_2(H_3C)N$$
$$6KHO \quad + \quad (H_3C)_3C_3N_3O_3 \quad = \quad 3K_2CO_3 \quad + \quad 3H_2(H_3C)N$$

γ. Its formation, also, by direct combination of hydrogen with prussic acid:

$$2H_2 \quad + \quad HCN \quad = \quad H_5CN \text{ or } H_2(H_3C)N$$

Prussic acid acted upon by nascent hydrogen, evolved from zinc and hydrochloric acid, and product distilled with potash; or mixed hydrogen gas and prussic acid vapour passed over platinum-black. Methylamine obtained as hydrochloride by condensing evolved gas in, or neutralising its aqueous solution with, hydrochloric acid, and evaporating down. Dry hydrochloride heated with quicklime, in long tube, lower half filled with mixture, and upper half with fragments of stick potash. Resulting gas collected over mercury. Methylamine a colourless, pungent, ammoniacal smelling gas, of sp. gr. $\frac{5+12+14}{2}=15{\cdot}5$. Its power of restoring blue colour of reddened litmus, of producing white fumes with hydrochloric acid, and of being largely absorbed by charcoal, water, and alcohol. Its solubility, 1150 volumes of methylamine in one volume of water at $12{\cdot}5$, greater than that of any other gas. Its condensation into liquid state, at a little below 0°. Its ready inflammability. Its behaviour with acids and anhydrides similar to that of ammonia. Its decomposition of most metallic salts to precipitate, and in some cases redissolve, hydrated oxides of respective metals. Its dissolution of chloride of silver, and decomposition of corrosive sublimate to form variety of white precipitate. Its reaction with iodine to form diniodo-methylamine as an unstable, but not explosive compound. Combination of hydrochloride of methylamine with chloride of platinum to form double salt $2ClH(H_5CN);Cl_4Pt$, analogous to $2ClH(H_3N);Cl_4Pt$.

Dimethylamine, H_7C_2N or $H(H_3C)_2N$; the least examined of the methylamines. Base produced as above described, by acting with methyl iodide upon ammonia or methylamine, and distilling resulting hydriodide with potash:

$$2IH_3C \quad + \quad 2H_3N \quad = \quad IH.H(H_3C)_2N \quad + \quad IH.H_3N$$

Dimethylamine separated from mono- and tri-methylamines by its reaction with oxalic ether to form oxal-dimethylamic ether, not volatilisable by heat of water-bath, soluble in cold water, and decomposible by potash with reproduction of dimethylamine. Base obtained in dry state by distillation of its dry hydrochloride

with potash. An ammoniacal smelling liquid, boiling at 8°, very soluble in water, forming strongly alkaline solution, neutralising acids, and decomposing metallic salts. Combination of hydrochloride of dimethylamine with chloride of platinum to form double salt, $2ClH(H_7C_2N);Cl_4Pt$.

Trimethylamine, H_9C_3N or $(H_3C)_3N$. Base met with under great variety of circumstances, and especially in stale herring brine. Produced by heating narcotine and other alkaloids with fused caustic potash; also, as above described, by action of methyl iodide upon ammonia, and distilling resulting hydriodide with potash:

$$3IH_3C \quad + \quad 3H_3N \quad = \quad IH(H_3C)_3N \quad + \quad 2(IH.H_3N)$$

Trimethylamine unaffected by oxalic ether, and obtained free from mono- and di-methylamine by its distillation in water-bath, after their fixation in forms of dimethyl-oxamide, and oxal-dimethylamic ether respectively. Base obtained in dry state by distillation of its dry hydrochloride with potash. Trimethylamine also produced by distillation of iodide and hydrate of tetramethylium. An oily, alkaline liquid, boiling at 9°, and yielding an inflammable vapour. Its characteristic odour of stale fish. Its free solubility in water, direct combination with acids, and decomposition of metallic salts. Its union with methyl iodide and ethyl iodide to form the iodides of tetramethylium and of ethyl-trimethylium respectively. Combination of its sulphate with sulphate of aluminium to form trimethylamine-alum $(H.H_9C_3N)'Al'''(SO_4)_2.12H_2O$, crystallising in octahedrons like the ammonia-salt $(H.H_3N)'Al'''(SO_4)_2.12H_2O$.

Tetramethylium-salts, &c. Iodide of tetramethylium the most abundant of the methyl products obtained by heating excess of methyl iodide with alcoholic ammonia in sealed tubes:

$$4IH_3C \quad + \quad 4H_3N \quad = \quad I(H_3C)_4N \quad + \quad 3(IH.H_3N)$$

On account of its sparing solubility, tetramethylium iodide readily purified by edulcoration with cold, and crystallisation from hot water. Its occurrence in hard, flat, brilliantly white needles,

having a very bitter taste. Its reaction with hydrated oxide of silver, to form insoluble iodide of silver, and solution of tetramethylium hydrate $HO.(H_3C)_4N$. Compound obtained in dry state by evaporating filtered solution in vacuo, over oil of vitriol. Residue very like caustic potash, white, crystalline, deliquescent, destructive of the cuticle, saponifacient, and absorptive of carbanhydride. Its neutralisation of acids to form salts, many of them isomorphous with corresponding potassium salts. Its precipitation of metallic solutions. Formula of its platinum salt $2Cl(H_3C)_4N; Cl_4Pt$.

Trimethyl-phosphine H_9C_3P, or $(H_3C)_3P$; a spontaneously inflammable, volatile liquid, corresponding in constitution to trimethylamine $(H_3C)_3N$, and to phosphoretted hydrogen H_3P. Its production by reaction of zinc methide and phosphorous chloride, in atmosphere of carbanhydride:

$$3(H_3C)_2Zn \quad + \quad 2Cl_3P \quad = \quad 3Cl_2Zn \quad + \quad 2(H_3C)_3P$$

Its neutralisation of acids to form salts, such as the hydrochloride $ClH(H_3C)_3P$. Its direct combination also with iodine, oxygen, and sulphur, and with disulphide of carbon, to form compounds $I_2(H_3C)_3P$, $(H_3C)_3PO''$, $(H_3C)_3PS''$, and $(H_3C)_3P.CS_2$. Reaction of hydrochloric acid with oxide of trimethyl-phosphine to form the chloride:

$$(H_3C)_3PO \quad + \quad 2HCl \quad = \quad Cl_2(H_3C)_3P \quad + \quad H_2O$$

Combination of trimethyl-phosphine with methyl iodide to form iodide of tetramethyl-phosphonium, as a white crystalline salt:

$$IH_3C \quad + \quad (H_3C)_3P \quad = \quad I(H_3C)_4P$$

Decomposition of its solution by hydrated oxide of silver, to form aqueous tetramethyl-phosphonium hydrate, as a strongly alkaline, bitter tasting liquid:

$$I(H_3C)_4P \quad + \quad AgHO \quad = \quad IAg \quad + \quad HO.(H_3C)_4P$$

The solid hydrate obtained by evaporation of above solution over oil of vitriol. Its great resemblance to caustic potash HOK. Analogy of methyl-phosphine to methyl-arsine, methyl-stibine, &c.

Boric methide, H_9C_3B, or $(H_3C)_3B$; a spontaneously inflammable gas, capable of fixation by ammonia to form ammonia-boric methide $(H_3C)_3B.H_3N$. Its production by reaction of zinc methide in ethereal solution, upon boracic ether:

$$3(H_3C)_2Zn \quad + \quad 2(EtO)_3B \quad = \quad 3(EtO)_2Zn \quad + \quad 2(H_3C)_3B$$

Evolved gas absorbed by ammonia, liberated on acidification of ammonia compound, and collected over mercury. A condensable, sparingly soluble, readily oxidisable gas, incapable of combining with chlorine or iodine, and having no tendency to unite with acids, but forming scarcely oxidisable compounds with ammonia and alkalis. Its spontaneous combustion in air, with a green flame and abundant black smoke.

Product of its gradual oxidation, apparently boric methide-dimethylate, $H_3C(H_3CO)_2B$ or $(H_3C)_3BO_2$, a compound having no analogy with the oxide of trimethyl-phosphine.

Silicic methide $H_{12}C_4Si$ or $(H_3C)_4Si$, made by acting with zinc methide upon silicic chloride, in sealed tubes heated to 200°:

$$2(H_3C)_2Zn \quad + \quad Cl_4Si \quad = \quad 2Cl_2Zn \quad + \quad (H_3C)_4Si$$

A colourless, mobile liquid, lighter than water, boiling at 30°, not spontaneously inflammable, but readily taking fire, and burning with a white flame and smoke of silica.

METAL METHIDES.

Direct or indirect replacement of chlorine by methyl in different metallic chlorides:

$(H_3C)Na$	$(H_3C)_2Zn''$	$(H_3C)_3As'''$	$(H_3C)_4Sn''''$
$ClNa$	Cl_2Zn''	Cl_3As'''	Cl_4Sn''''

Replacement of chlorine by methyl in successive stages, illustrated by methyl-arsenious compounds:

$$Cl_3As, \qquad Cl_2(H_3C)As, \qquad Cl(H_3C)_2As, \qquad (H_3C)_3As$$

Metal methides procurable by various processes.

α. Direct combination of some metals with methyl iodide, under exposure to sunlight, or with aid of heat and pressure, to form methyl-iodides, as of mercury $I(H_3C)Hg$, of zinc $I(H_3C)Zn$, of tin $I_2(H_3C)_2Sn$, &c. Decomposition of zinc methyl-iodide by heat into zinc methide and zinc iodide:

$$2I(H_3C)Zn \quad = \quad I_2Zn \quad + \quad (H_3C)_2Zn$$

β. Reaction of iodide, potassio-sulphate, &c. of methyl with sodium- or potassium- alloy of mercury, arsenic, antimony, bismuth, tellurium, tin or lead:

$$3I(H_3C) \quad + \quad Na_3Sb \quad = \quad 3INa \quad + \quad (H_3C)_3Sb$$

γ. Double decomposition of halide or methyl-halide of one metal with methide of another metal:

$$(H_3C)_2Zn \quad + \quad I_2(H_3C)_2Sn \quad = \quad I_2Zn \quad + \quad (H_3C)_4Sn$$

δ. Replacement of less basylous by more basylous metal, as of mercury by aluminium:

$$3(H_3C)_2Hg \quad + \quad Al_2 \quad = \quad (H_3C)_6Al_2 \quad + \quad Hg_3$$

Monad-metal methides.—Sodium methide $(H_3C)Na$, and potassium methide $(H_3C)K$, known only in combination with zinc methide, mercury methide, &c. Made by acting on zinc- or mercury methide with alkali-metal. Their absorption of carbanhydride to form acetates:

$$NaH_3C \quad + \quad CO_2 \quad = \quad NaH_3C_2O_2$$

Diad-metal methides.—Zinc methide $(H_3C)_2Zn$, producible by processes *α* and *δ*. A spontaneously inflammable liquid, boiling between 50° and 60°. Its reaction with iodine at two stages to form zinc methyl-iodide, and zinc iodide, successively:

$$(H_3C)_2Zn \quad + \quad I_2 \quad = \quad I(H_3C)Zn \quad + \quad I(H_3C)$$
$$I(H_3C)Zn \quad + \quad I_2 \quad = \quad I_2Zn \quad + \quad I(H_3C)$$

Its absorption of oxygen to form zinc methide-methylate $H_3C(H_3CO)Zn$, and zinc methylate $(H_3CO)_2Zn$, successively. Its

reaction with water to form zinc hydrylate, and with ammonia to form zinc amide:

$$(H_3C)_2Zn \quad + \quad 2H_2O \quad = \quad (HO)_2Zn \quad + \quad 2H(H_3C)$$

Its reactions with chloride of phosphorus, boracic ether, &c., already illustrated.

Mercury methide $(H_3C)_2Hg$, producible by processes β and γ. The methyl-iodide formed according to α, by exposing mercury covered with methyl iodide to sunlight. Mercury methide a colourless extremely heavy liquid, boiling at 93°, very slowly oxidisable, unacted upon by and insoluble in water. Its decomposition by sodium, zinc, aluminium, &c., with extrusion of mercury. Characteristic tendency of mercury methide to retain one proportion of methyl with considerable tenacity, and exchange the other proportion for any simple or compound acid-radical, so as to form salts, such as the iodide $I(H_3C)Hg$, chloride $Cl(H_3C)Hg$, hydrate $(H_3C)Hg.HO$, nitrate $(H_3C)Hg.NO_3$, &c. &c. Its reactions with iodine, hydrochloric acid, and corrosive sublimate respectively:

$$(H_3C)_2Hg \quad + \quad I_2 \quad = \quad I(H_3C)Hg \quad + \quad IH_3C$$
$$(H_3C)_2Hg \quad + \quad ClH \quad = \quad Cl(H_3C)Hg \quad + \quad H.H_3C$$
$$(H_3C)_2Hg \quad + \quad Cl_2Hg \quad = \quad 2Cl(H_3C)Hg$$

Reaction of mercury-methyl-chloride and -methyl-iodide with nitrate and hydrate of silver to form the methyl-nitrate and methyl-hydrate of mercury. Mercury methyl-hydrate a soluble alkaline liquid, neutralising acids to form salts:

$$(H_3C)Hg.HO \quad + \quad HNO_3 \quad = \quad (H_3C)Hg.NO_3 \quad + \quad H_2O$$

Triad-metal methides.—Aluminium methide $(H_3C)_3Al$, or $(H_3C)_6Al_2$, best made by process δ. A spontaneously inflammable liquid, boiling at 130°, and freezing into a mass of white tabular crystals at a little above 0°. Its reaction with iodine to form aluminium methyl-iodide, probably $I_2(H_3C)Al$.

Tetra-diad-metal methides.—Combination of tellurium and tin with methyl to form the unsaturated compounds $(H_3C)_2Te$ and $(H_3C)_2Sn$. Direct union of these methides with iodine to

form tetrad compounds such as $I_2(H_3C)_2Sn$, in contradistinction to double decomposition with iodine of previously considered zinc- and mercury methides. Tellurous and stannous methides comparatively unimportant. Existence of stannic methide and two out of the three intermediate stannic methyl-iodides:

$$I_4Sn \qquad \mathit{I_3(H_3C)Sn} \qquad I_2(H_3C)_2Sn \qquad I(H_3C)_3Sn \qquad (H_3C)_4Sn$$

Compounds made by processes α, β, and γ. Stannic methide a thin heavy oil, boiling at 140°—145°. Its reaction with iodine to form stannic methyl-iodide:

$$(H_3C)_4Sn + I_2 = I(H_3C)_3Sn + IH_3C$$

The above iodide, and the diniodide $I_2(H_3C)_2Sn$, volatile compounds, the former oily, the latter solid, at ordinary temperatures. Replacement in each compound, of iodine by some other radical, to form the hydrate $(H_3C)_3Sn.HO$, sulphate $(H_3C)_2Sn.SO_4$, &c. &c. The two hydrates or oxides, basic substances, capable of neutralising acids to form various salts, for the most part crystallisable.

Lead methide $(H_3C)_4Pb$, best made according to process γ, by reaction of lead chloride and zinc methide:

$$2(H_3C)_2Zn + 2Cl_2Pb = 2Cl_2Zn + (H_3C)_4Pb + Pb$$

A colourless, heavy, not particularly oxidisable liquid, boiling at 100°. Its reactions with iodine and hydrochloric acid to form lead methyl-iodide and lead methyl-chloride, respectively:

$$(H_3C)_4Pb + I_2 = I(H_3C)_3Pb + IH_3C$$
$$(H_3C)_4Pb + HCl = Cl(H_3C)_3Pb + H_4C$$

Formation from these compounds of the hydrate, $(H_3C)_3Pb.HO$, as a basic oil.

Penta-triad-metal methides. Arsen-methides or methylarsines. Series of arsenic and arsenious compounds.

	Arsenic	Arsenious	
A	$I(H_3C)_4As$	$(H_3C)_3As$	*a*
B	$Cl_2(H_3C)_3As$	$Cl(H_3C)_2As$	*b*
C	$Cl_3(H_4C)_2As$	$Cl_2(H_3C)As$	*c*
D	$Cl_4(H_3C)As$	Cl_3As	*d*

Each arsenious compound, except *b*, produced, together with methyl halide, by distillation of corresponding arsenic compound. Arsenious compound *b* producible from kakodyl.

Each arsenic compound, except *A*, producible from preceding arsenious compound by its combination with halogen. Arsenic methyl-iodide or iodide of methyl-arsonium (*A*), produced according to process β, by action of iodide of methyl on arsenide of sodium Na_3As.

The tri- and tetra-methyl arsen-compounds very similar to their analogues in the phosphorus and antimony series.

Special interest of dimethyl arsen-, or so called kakodyl compounds.

		$Cl(H_3C)_2\overset{'''}{As}$	Chloride of kakodyl
		$Cl_3(H_3C)_2\overset{\mathrm{v}}{As}$	Trichloride of kakodyl
$O''\left\{\begin{array}{l}H_3C)_2As\\ H_3C)_2As\end{array}\right.$	or	$O''(H_3C)_4\overset{'''}{As}_2$	Oxide of kakodyl
		$(H_3C)_4\overset{'''}{As}_2$	Kakodyl
$HO(H_3CO)H_3C.As$	or	$H(H_3C)_2\overset{'''}{As}O_2$	Kakodylic acid
		$ClH_2(H_3C)_2\overset{\mathrm{v}}{As}O_2$	Hydrochloride of Kd. acid

Alkarsin,—a spontaneously inflammable, volatile, highly poisonous liquid, composed of kakodyl oxide with some kakodyl,—the prime source of kakodyl compounds. Its production by distillation of mixture of arsenious oxide with acetate of potassium. Kakodyl oxide obtained by cautious exposure of alkarsin to air, and distillation of product with water, so as to carry over oxide of kakodyl, and leave kakodylic acid. Oxide of kakodyl a heavy oil, not inflammable or fuming in air, but oxidisable by exposure into kakodylic acid. Its boiling point 120°. Its union with corrosive sublimate to form compound $O''(H_3C)_4As_2; 2Cl_2Hg$. Kakodylic acid obtainable as above, and purified by crystallisation from alcohol. Its difference from other kakodyl compounds in being innocuous, though containing 54·35 per cent of arsenic. A well characterised stable acid, unalterable by heat of 200°. Its combination with strong aqueous hydrochloric acid to form the hydrochloride, left on evaporation in vacuo as a crystalline mass.

Kakodyl chloride made by distilling the oxide, or preferably its corrosive sublimate compound, with hydrochloric acid:

$$O''(H_3C)_4As_2 \quad + \quad 2HCl \quad = \quad 2Cl(H_3C)_2As \quad + \quad H_2O$$

A heavy mobile liquid, boiling at a little over 100°, and yielding an inflammable vapour. Its spontaneous combustion in chlorine, but conversion by gradual action of chlorine into the trichloride $Cl_3(H_3C)_2As$,—a crystalline compound breaking up at a gentle heat into arsenious methyl-dichloride, and chloride of methyl:

$$Cl_3(H_3C)_2As \quad = \quad Cl_2(H_3C)As \quad + \quad ClH_3C$$

Kakodyl a volatile, very offensive, highly poisonous, spontaneously inflammable liquid, formed by action of zinc upon chloride of kakodyl, and isolable only by employment of special precautions:

$$2Cl(H_3C)_2As \quad + \quad Zn \quad = \quad (H_3C)_4As_2 \quad + \quad Cl_2Zn$$

Its crystallisation at $-6°$, ebullition at 170°, and evolution of vapour at ordinary temperatures. Its conversion, by gradual action of air, into oxide of kakodyl, and kakodylic acid, and its reconversion by chlorine water into chloride of kakodyl. Its explosive inflammation with chlorine.

Methyl-stibine, H_9C_3Sb or $(H_3C)_3Sb$, producible like methyl-phosphine and methyl-arsine according to processes β and γ, by action of methyl iodide upon antimonide of sodium, or of zinc methide upon chloride of antimony. A heavy, volatile, fuming, spontaneously inflammable liquid. Its direct combination with iodine to produce the iodide, and decomposition of hydrochloric acid to produce the chloride:

$$(H_3C)_3Sb \quad + \quad 2HCl \quad = \quad Cl_2(H_3C)_3Sb \quad + \quad H_2$$

The oxide $(H_3C)_3SbO''$, obtainable by cautious exposure of methyl-stibine to air, and in other ways. A basic substance, neutralising acids to form salts, as the nitrate $(H_3C)_3Sb(NO_3)_2$. Combination of methyl iodide with methyl-stibine to form the iodide of methyl-stibonium $I(H_3C)_4Sb$, as a very finely crystallised

salt. Liberation of iodine from it by all oxidising agents, including ozone. Decomposition of its solution by hydrated oxide of silver, with formation of hydrate of methyl-stibonium, obtainable in solid state by evaporation of liquid in vacuo. Its great resemblance to caustic potash, shown by its strongly alkaline reaction; by its evolution of ammonia from ammonia salts, even in the cold; by its absorption of carbanhydride from the air; by its precipitation of metallic salts, with re-solution of some of the precipitates; by its neutralisation of acids to form soluble salts; and by its solution of sulphur at a gentle heat, to form an orange liquid, decomposible by acids, with precipitation of sulphur and evolution of sulphuretted hydrogen.

Bismuth methide $(H_3C)_3Bi$, unknown. The ethide $(H_5C_2)_3Bi$, similar in formation and properties to ethyl-stibine $(H_5C_2)_3Sb$ and methyl-stibine $(H_3C)_3Sb$, though less readily oxidisable, and not susceptible of distillation save in vapour of water. Its combination with ethyl iodide to form the iodide $I(H_5C_2)_4Bi$. Reaction of bismuth ethide with corrosive sublimate to form the ethyl-dichloride:

$$Et_3Bi + 2Cl_2Hg = Cl_2EtBi + 2ClEtHg$$

Indirect replacement of chlorine in above compound by other acid radicals, to form various salts of bismuth mon-ethyl.

(50.) Formio-Carbonic Compounds.

Form-aldehyd H_2CO, the oxygen representative of marsh-gas H_4C, obtained in alcoholic solution by direct oxidation of methyl alcohol:

$$H_4CO + O = H_2CO + H_2O$$

Current of air, charged with methyl alcohol vapour, passed over coil of heated platinum wire, and then through condenser. Resulting solution of aldehyd a characteristically pungent-smelling liquid, absorbing oxygen from the air to yield formic acid, becoming resinified by potash, and reducing ammonio-nitrate of silver with production of brilliant metallic mirror. Formic

sulphaldehyd H_2CS, produced by treating above solution with sulphuretted hydrogen gas, adding hydrochloric acid, heating mixture to boiling point, and setting aside:

$$H_2CO + H_2S = H_2CS + H_2O$$

Deposition of brilliant white interlaced crystals, slightly soluble in water, more so in alcohol, and still more so in ether.

Correspondence of formic and methylic compounds:

$H.H_3C$	Methene	$H.HCO$	Form-aldehyd
$HO.H_3C$	Methyl alcohol	$HO.HCO$	Formic acid
$H_2N.H_3C$	Methylamine	$H_2N.HCO$	Formiamide

Formic chloride $Cl.HCO$, unknown. Formic anhydride $(HCO)_2O$, the analogue of methyl ether $(H_3C)_2O$, also unknown. Existence of intermediate formic methyl-ether $H_3C(HCO)O$. Dehydrated formic acid, or carbonous oxide CO, analogous to the unknown methylen H_2C, and phosgene Cl_2CO, analogous to chloride of methylen Cl_2H_2C.

In marsh gas H_4C, only one of the atoms of hydrogen replaceable by hydroxyl, to furnish methyl alcohol $HO.H_3C$, corresponding to methylamine $H_2N.H_3C$; but in formic aldehyd H_2CO, one or both atoms of hydrogen replaceable by hydroxyl to produce either formic acid $HO.HCO$, corresponding to formiamide $H_2N.HCO$, or carbonic acid $(HO)_2CO$ corresponding both to carbamic acid $HO(H_2N)CO$, and to carbamide $(H_2N)_2CO$. The four atoms of hydrogen in marsh gas H_4C, replaceable by oxygen to form carbanhydride CO_2.

(51) Formic Acid, etc.

Carbonous oxide CO, a product of destructive distillation of organic substances. *a.* Gas obtained by reduction of carbanhydride in various ways, as by heating to redness a mixture of chalk with zinc, iron, charcoal, &c.:

$$CaO.CO_2 + Zn = CaO + ZnO + CO$$

Or by imperfect oxidation of carbon at high temperatures, as by

its ignition with deficit of oxide of copper, peroxide of manganese, oxygen of air, &c., or in current of steam or carbanhydride. Probable formation and subsequent reduction of carbanhydride in most such actions, thus:

$$2H_2O + C = CO_2 + H_4$$
$$CO_2 + C = 2CO$$

β. Production also of carbonous oxide by action of sulphuric acid upon formic or oxalic acid, with elimination of water,

$$H_2CO_2 = H_2O + CO$$
$$H_2C_2O_4 = H_2O + CO + CO_2;$$

or upon hydrocyanic acid with absorption of water:

$$H_2O + HCN + H_2SO_4 = CO + H_3N.H_2SO_4$$

In practice, the double cyanide of potassium and iron $K_4Fe''(CN)_6.3H_2O$ (yellow prussiate of potash), substituted for cyanide of hydrogen. Formic acid process not used. Absorption of carbanhydride, resulting from oxalic acid process, by means of potash or lime.

Carbonous oxide a neutral, permanent, sparingly soluble, highly poisonous gas, burning in air or oxygen with characteristic blue flame to form carbanhydride. Its combination with oxygen, producible by intervention of platinum-black. Its value as a deoxidising agent in metallurgical processes. Its combination with chlorine under exposure to sunlight, or when in nascent state, to produce phosgene Cl_2CO. Its absorption by potassium to yield definite compound $K_2(CO)_2$. Also by heated caustic potash, with gradual production of formiate:

$$KHO + CO = KHCO_2$$

Solubility of carbonous oxide gas in ammoniacal and hydrochloric acid solutions of cuprous salts.

Formic acid H_2CO_2. Its occurrence in juices of red ants, stinging nettles, and other animal and vegetable bodies; and as a product of the artificial oxidation of many organic substances by various processes. Its formation for instance from alcohol,

in process for making chloroform, and through intervention of chloral and chloracetic acid, by their decomposition with potash: also from woody fibre, starch, sugar, tartaric acid, gelatin, &c., by their oxidation with sulphuric acid and peroxide of manganese or red chromate of potassium. Acid frequently made by distilling a mixture of starch, peroxide of manganese, water, and sulphuric acid.

Production of formic acid from other monocarbon compounds. From marsh-gas by decomposition of its derivative chloroform with potash; from methyl alcohol by its transmission over heated soda-lime, or direct oxidation with air, under influence of platinum black; from carbonous oxide by its gradual combination with caustic potash heated to 100° for forty-eight hours; from carbonic acid by its reduction with metallic sodium; and from hydrocyanic acid by its decomposition with potash:

$$2H_2O \quad + \quad HCN \quad = \quad H_2CO_2 \quad + \quad H_3N$$

Manufacture of formic acid by decomposition of oxalic acid, at a moderate heat:

$$H_2C_2O_4 \quad = \quad H_2CO_2 \quad + \quad CO_2$$

Oxalic acid preferably mixed with glycerin, and mixture gently heated for some time until cessation of effervescence. Residue then diluted with water, and formic acid distilled off. Distillate neutralised with carbonate of lead, resulting formiate of lead decomposed with sulphuric acid, and product distilled off fresh lead formiate:

$$Pb(HCO_2)_2 \quad + \quad H_2SO_4 \quad = \quad 2H_2CO_2 \quad + \quad PbSO_4$$

Formic acid a thin, sour, pungent, corrosive, inflammable liquid, miscible with water in all proportions, and forming a definite hydrate $H_2CO_2.H_2O$. Its sp. gr. 1·235, freezing point $-1°$, and boiling point 100°. Its dehydration by strong sulphuric acid, with production of carbonous oxide:

$$H_2CO_2 \quad = \quad H_2O \quad + \quad CO$$

Its ready conversion into carbonic acid by all oxygenants, in-

cluding oxide of mercury, peroxide of manganese, moist chlorine, &c.; whence its use as a powerful reducing agent, as upon salts of silver, mercury, gold and platinum:

$$HgO + H_2CO_2 = Hg + H_2CO_3 \text{ or } H_2O.CO_2$$

Result of its ignition with caustic alkali or alkaline earth, the production of hydrogen and carbanhydride; or hydrogen and oxalic acid; or water, marsh-gas, and carbanhydride, according to circumstances:

$$H_2CO_2 = H_2 + CO_2$$
$$2H_2CO_2 = H_2 + H_2C_2O_4$$
$$4H_2CO_2 = 2H_2O + H_4C + 3CO_2$$

Formiates.—Soluble crystallisable salts, made by dissolving metallic hydrates, oxides, or carbonates in formic acid. The sodium salt $NaHCO_2$, which also crystallises with an atom of water, barium salt $Ba''(HCO_2)_2$, and lead salt $Pb''(HCO_2)_2$, the best known compounds. A few double or acid formiates as $NaHCO_2.H_2CO_2$, made by dissolving monad formiates in hot formic acid. Dehydration of ammonia formiate into formiamide and formionitrile successively (*vide infra*). Reaction of most formiates with ferric solutions, to produce deep red ferric formiate. Similar effect of oil of vitriol, oxygenants, and ignition, upon formiates, as upon formic acid.

Formic ethers.—Methyl formiate, $(H_3C)HCO_2$ or $H_3C(HCO)O$, and ethyl formiate, $(H_5C_2)HCO_2$ or $H_5C_2(HCO)O$, &c. well defined compounds, made by distilling sodium formiate with mixture of sulphuric acid and methyl- or ethyl- alcohol, *i.e.* with sulphate or hydrogen-sulphate of methyl or ethyl:

$$2NaHCO_2 + (H_3C)_2SO_4 = 2(H_3C)HCO_2 + Na_2SO_4$$

Neutral volatile liquids, decomposible by caustic alkali into formiate and alcohol, and yielding chlorine substitution-products. Perchloro-methyl-formiate $(Cl_3C)ClCO_2$ or $Cl_4C_2O_2$ transformable into phosgene by transmission through heated tubes:

$$Cl_4C_2O_2 = 2Cl_2CO$$

Its action upon alcohol identical with that of phosgene.

Formic amide or formiamide $H_2N.HCO$, obtainable by heating formic ether with dry ammonia in sealed tubes:

$$H_3N \quad + \quad \left.\begin{matrix}Et\\HCO\end{matrix}\right\}O \quad = \quad H_2N.HCO \quad + \quad HEtO$$

Also by carefully heating formiate of ammonia:

$$H_3N.H_2CO_2 \quad = \quad H_2N.HCO \quad + \quad H_2O$$

A colourless, volatile liquid, distillable without alteration in a partial vacuum, but decomposing, when heated under ordinary pressure, into water and formic-nitrile or prussic acid:

$$H_2N.HCO \quad = \quad NHC \quad + \quad H_2O$$

(52.) Carbonic Acid, etc.

Carbonic acid viewed as dihydrate of carbonyl, or of carbon half saturated by oxygen $(HO)_2CO$. Existence of corresponding chloride, amide, and intermediate compounds:

$(CO)Cl_2$	or	$(CO)\left\}\begin{matrix}Cl\\Cl\end{matrix}\right.$	Phosgene gas	Cl_2CO
$H(CO)OCl$	or	$\left.\begin{matrix}(CO)\\H\end{matrix}\right\}\begin{matrix}Cl\\O\end{matrix}$	Chloro-carb. acid	$Cl(HO)CO$
$H_2(CO)O_2$	or	$\left.\begin{matrix}H\\(CO)\\H\end{matrix}\right\}\begin{matrix}O\\O\end{matrix}$	Carbonic acid	$(HO)_2CO$
$\left.\begin{matrix}H_2\\H(CO)\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$	or	$\left.\begin{matrix}H_2\\(CO)\\H\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$	Carbamic acid	$HO(H_2N)CO$
$H_4(CO)N_2$	or	$\left.\begin{matrix}H_2\\(CO)\\H_2\end{matrix}\right\}\begin{matrix}N\\N\end{matrix}$	Carbamide	$(H_2N)_2CO$

Oxalic and mesoxalic compounds, constituted in a similar manner with radicals dicarbonyl or oxalyl, and tricarbonyl or mesoxalyl respectively, as illustrated by formulæ for acids or hydrates:

H_2CO_3	Carbonic	$(HO)_2CO$
$H_2C_2O_4$	Oxalic	$(HO)_2C_2O_2$
$H_2C_3O_5$	Mesoxalic	$(HO)_4C_3O_3$

Dehydration of carbonic, as of other dibasic acids, by abstraction from its single molecule of one atom of water:

$$H_2CO_3 \quad - \quad H_2O \quad = \quad CO_2$$

Through its spontaneous dehydration, carbonic acid **known only in state** of aqueous **solution, but** well **represented by its** different **salts** and ethers; **and also by sulphocarbonic acid** H_2CS_3. Carbonic acid and anhydride the first terms respectively of two homologous series of acids and anhydrides:

$H_2C\,O_3$	Carbonic	$C\,O_2$	Carbanhydride
$H_4C_2O_3$	Glycolic	$H_2C_2O_2$	Glycolide
$H_6C_3O_3$	Lactic	$H_4C_3O_2$	Lactide
"	"	"	"
$H_{12}C_6O_3$	Leucic	$H_{10}C_6O_2$	Leucide

Existence of various sulphocarbonic compounds, illustrated by Cl_2CS, H_2CS_3, CS_2, &c.

CARBONIC ACID.

Carbonic dioxide or anhydride, CO_2. Its occurrence in the atmosphere to extent of 0·4 per cent. by volume. Its origin from earth-fissures, mineral springs, &c.; from the processes of combustion, respiration, decay or eremacausis, germination, &c.; and from lime-burning. Its existence in expired air to the extent of about 3·5 per cent.; and in air of crowded and gas-lighted rooms to the extent of not more than 0·5 per cent. Importance of carbanhydride, both as the chief source and chief product of metamorphosis of organic tissues, vegetal and animal.

a. Its production by combustion of carbon and carbonaceous substances in air or oxygen.

β. Its production from carbonates, by their ignition either alone or with some fixed anhydride:

$$CaCO_3 \quad = \quad CaO \quad + \quad CO_2;$$

or by their decomposition with acids:

$$CaCO_3 \quad + \quad 2HCl \quad = \quad CaCl_2 \quad + \quad H_2O \quad + \quad CO_2$$

Gas made on a large scale by action of sulphuric acid on mixture of chalk and water; in laboratories, by action of dilute hydrochloric acid on marble.

γ. Its frequent occurrence as a product of the decomposition of organic acids by heat, and of various decompositions of organic compounds in general.

Carbanhydride a colourless, inodorous, almost tasteless gas. Its extinction of combustion and of life. Accidents from evolution of carbanhydride in wells, caverns, fermenting vats, lime-kilns, &c. Its action, even when much diluted, as a narcotic. Specific gravity of gas, $\frac{12 + 16 \times 2}{2} = 22$, or one and a half times that of air (1·524 Regnault). Its collection by downward displacement, and capability of being poured through air. Variation in its coefficients of compressibility, and of dilatability by heat, at low temperatures. Its liquefaction, by pressure of 38·5 atmospheres at 0°. Production of liquid carbanhydride on a large scale, from decomposition by sulphuric acid of hydro-sodium carbonate $HNaCO_3$, in Thilorier's or Natterer's apparatus. Gas generated under pressure in (or afterwards compressed into) iron cylinders. A thin, colourless, liquid of sp. gr. 0·83 at 0°, immiscible with water, miscible in all proportions with alcohol, ether, and essential oils. Its general resemblance to disulphide of carbon. Its great expansibility by heat. Solid carbanhydride usually produced as a snow-white flocculent mass, by spontaneous evaporation of stream of liquid anhydride escaping under pressure. Its low temperature, −77°, maintained by constant volatilisation. Its capability, nevertheless, of being handled, &c., owing to an absence of contact, by reason of its volatilisation. Its comparative permanence when surrounded by non-conducting materials. Employment of solid carbanhydride, wetted with ether, as a frigorific agent; readily capable of freezing mercury. Freezing or melting point of mercury −39°. Depression of temperature to −110°, by volatilisation of solid carbanhydride and ether under receiver of air-pump. Production of carbanhydride in form of ice, by cooling the liquid, in a bath of the solid anhydride and ether.

Its melting point $-57°$. Precipitation by carbanhydride gas of lime-water, baryta-water, basic acetate of lead solution, &c., with formation of carbonates. Its partial decomposition into carbonous oxide and oxygen, by transmission through it of electric sparks. Its reduction to state of carbonous oxide, by ignition with hydrogen, iron, zinc, &c.:

$$CO_2 + H_2 = CO + H_2O$$

Its partial reduction to state of carbon, by combustion in it of potassium, sodium, phosphorus, &c.:

$$3CO_2 + Na_4 = 2Na_2CO_3 + C$$

Absorption of carbonic anhydride or acid from the atmosphere by growing plants, exposed to sunlight, with fixation of carbon and evolution of oxygen.

Carbonic acid, H_2CO_3. Solubility at ordinary temperatures of one volume of carbanhydride in one volume of water. Bulk of gas absorbed almost independent of, and its weight directly proportionate to, pressure, in approximate accordance with Henry and Dalton's law. Excess of dissolved gas evolved on removal of pressure. Complete solution and evolution of gas, gradual. Variation of solubility of carbanhydride inversely as temperature. Its complete discharge by ebullition; also by congelation.

Aqueous solution of carbanhydride characterised by a sharp taste, faintly acid reaction, power of neutralising alkalis, of dissolving iron, &c., with evolution of hydrogen, of retaining calcium carbonate, phosphate, &c. in solution, and of liberating feeble acids from their combinations. The acid resulting from union of carbonic anhydride and water not isolable; formulated as H_2CO_3, by analogy, and from constitution of carbonates. Moist carbanhydride gas, or carbonic acid, rendered anhydrous by ordinary desiccating agents. Action of aqueous carbonic acid on lime-water to precipitate chalk. Solubility of chalk in excess of carbonic acid, with production of an acid carbonate:

$$CaCO_3 + H_2CO_3 = Ca(HCO_3)_2$$

Reprecipitation of chalk by ebullition. Furring of steam boilers from deposition of earthy carbonates, &c., originally held in solution by carbonic acid of the water. Partial reduction of carbonic acid, by metallic sodium, to state of formiate:

$$2H_2CO_3 \quad + \quad Na_2 \quad = \quad NaHCO_3 \quad + \quad NaHCO_2 \quad + \quad H_2O$$

Carbonates. Normal salts formed on the type of carbonic acid H_2CO_3. Formulæ of the most important simple carbonates shown below:

Monadic	Diadic	
$(NH_4)HCO_3.2Aq$	$CaCO_3$	Calc-spar. Arragonite
$NaHCO_3$	$SrCO_3$	Strontianite
$KHCO_3$	$BaCO_3$	Witherite
Li_2CO_3	$PbCO_3$	Cerusite
$Na_2CO_3.10Aq$	$MgCO_3$	Talc-spar. Magnesite
$K_2CO_3.2Aq$	$ZnCO_3$	Zinc-spar. Calamine
$KNaCO_3.6Aq$	$FeCO_3$	Iron-spar. Siderite
Ag_2CO_3	$MnCO_3$	Brown-spar. Diallage

The monad carbonates, except carbonate of silver, soluble crystalline salts, those with two atoms of metal being alkaline, and those with one atom of metal, neutral, or nearly so. Carbonate of lithium but sparingly soluble, however.

The diad carbonates insoluble, and found native as crystalline minerals. Precipitation by alkali carbonates of calcium, strontium, barium, and lead salts, as normal carbonates; and of magnesium, zinc, iron, and manganese salts as basic carbonates. The moist precipitates soluble in excess of carbonic acid water, probably in form of hydrocarbonates, as $Ca(HCO_3)_2$, $Fe(HCO_3)_2$, &c. The so dissolved carbonates deposited from solution, on evolution of carbanhydride, sometimes in crystalline state.

Existence of many complex and basic carbonates as natural or artificial compounds. Most important basic salts formulated below. Their representation either as double hydrate-carbonates, or as ortho-carbonates analogous to orthosilicates.

$Ca_2\ddot{O}CO_3$	or	Ca_2CO_4	Half burned lime
$Ca_2(HO)_2CO_3$	„	$Ca_2CO_4.H_2O$	Air slaked lime
$Zn_2(HO)_2CO_3$	„	$Zn_2CO_4.H_2O$	Schindler's salt
$Pb_2(HO)_2CO_3$	„	$Pb_2CO_4.H_2O$	Bonsdorff's salt
$Cu_2(HO)_2CO_3$	„	$Cu_2CO_4.H_2O$	Malachite
$Cu\ddot{O}CO_3$	„	Cu_2CO_4	Mysorine
$Cu_3(HO)_2(CO_3)_2$	„	$H_2Cu_3(CO_4)_2$	Azurite
$Pb_3(HO)_2(CO_3)_2$	„	$H_2Pb_3(CO_4)_2$	White lead
$Mg_4(HO)_2(CO_3)_3$	„	$\left\{\begin{matrix} H_2Mg_3(CO_4)_2 \\ MgCO_3 \end{matrix}\right\}$	Hydromagnesite

Carbonates of heavy metals and of earth-metals proper decomposible by a red heat. Among alkali-metal carbonates, that of calcium decomposible by a full red heat, that of barium only at an intense white heat, and that of strontium at an intermediate temperature. Decomposition facilitated by admixture of carbonates with carbon, to transform acidulous carbanhydride into neutral carbonous oxide:

$$BaCO_3 \quad + \quad C \quad = \quad BaO \quad + \quad 2CO$$

Alkali-metal carbonates undecomposible by heat alone. That of lithium decomposed to a considerable extent, and that of sodium to a small extent, by strong ignition in a current of air. The decomposition even of potassium and barium carbonates producible, to a greater or less extent, by their strong ignition in a current of steam. All carbonates decomposed by ignition with excess of fixed anhydride, or anhydro-salt. Their decomposition at ordinary or slightly increased temperatures by aqueous acids, with evolution of carbonic acid or anhydride.

Abundant existence in nature of calcium carbonate as chalk, limestone, and marble; of magnesium carbonate as magnesite and dolomite; of iron carbonate as spathic iron ore and clay iron stone; of copper carbonate as malachite; and of zinc carbonate as calamine. Carbonate of potassium, and formerly carbonate of sodium, produced by ignition of land and marine plants respectively. Carbonate of sodium now made by ignition of sulphate

of sodium with mixture of chalk and coal. Carbonate of ammonia made by sublimation of sulphate or chloride of ammonium with chalk. Carbonate of lead made by action of carbonic acid on basic acetate of lead. The acid or hydrogen carbonates made by action of carbonic acid on preformed carbonates.

Carbonic ethers. Compounds formed by indirect action of carbonic acid upon alcohol, and regarded as derivatives of carbonic acid by substitution of methyl or ethyl, &c. for hydrogen. Ethyl-carbonate of potassium $KEtCO_3$, produced as a crystalline precipitate by passing carbanhydride into alcoholic solution of caustic potash:

$$KHO + EtHO + CO_2 = KEtCO_3 + H_2O$$

Its decomposition by ethyl-sulphate or methyl-sulphate of potassium, to form carbonic ether or methyl-ethyl carbonic ether:

$$KEtSO_4 + KEtCO_3 = K_2SO_4 + Et_2CO_3$$

Carbonic ether also made according to a complex reaction, by decomposing oxalic ether with metallic sodium. Carbonic ether a colourless inflammable liquid, boiling at 125°, insoluble in water, freely soluble in alcohol and ether. Its decomposition by alcoholic potash to form potassium carbonate and alcohol. Its reaction with ammonia to form carbamic ether or urethane, together with some carbamide or urea:

$$H.H_2N + Et_2CO_3 = HEtO + \left.\begin{matrix} H_2 \\ Et(CO) \end{matrix}\right\} \begin{matrix} N \\ O \end{matrix}$$

Its conversion by chlorine into perchloro-carbonic ether $(Cl_5C_2)_2CO_3$ or $Cl_{10}C_5O_3$.

SULPHOCARBONATES, ETC.

Disulphide of carbon. *Sym.* CS_2; *p. n.* 76; produced by the combustion of carbon in sulphur vapour. Its manufacture on a large scale by allowing sulphur, vaporised by contact with red-hot brick-work, to pass over masses of coke, strongly ignited in upright furnaces, and condensing the product. Disulphide of carbon when pure, a colourless refringent liquid, having an offensive alliaceous smell, a sp. gr. of 1·271, and

boiling point 46·6°. Its free vaporisation at ordinary temperatures, with production of cold. Its insolubility in water, solubility in alcohol, ether, and liquid hydrocarbons. Its employment as a solvent for bitumens, resins, caoutchouc, and all sorts of fatty substances. Its free dissolution of phosphorus, sulphur, and iodine. Bright crimson or pink colour of disulphide of carbon solution of iodine, made use of as a test for iodine. Combustibility of disulphide of carbon vapour, even at very low temperatures, as 150°, with characteristic blue flame. Its explosion, when fired in admixture with air or oxygen. Its quiet but very brilliant combustion in admixture with nitric oxide. Its reactions with oxide of hydrogen or metal, at various low temperatures, to produce sulphides, together with carbonic acid or anhydride. Some sulphides, not formed in moist way, as of aluminium, obtainable by this reaction:

$$2H_2O \quad + \quad CS_2 \quad = \quad 2H_2S \quad + \quad CO_2$$
$$2Al_2O_3 \quad + \quad 3CS_2 \quad = \quad 2Al_2S_3 \quad + \quad 3CO_2$$

Its decomposition by many metals at a red heat, so as to produce metallic sulphides and a deposit of carbon. Its joint reaction with sulphuretted hydrogen upon metallic copper, to yield a small proportion of marsh-gas:

$$Cu_8 \quad + \quad 2H_2S \quad + \quad CS_2 \quad = \quad 4Cu_2S \quad + \quad H_4C$$

Its various reactions with chlorine, to produce the compounds Cl_2CS, Cl_4CSO_2, and Cl_4C, according to circumstances.

Its solubility in aqueous solutions of alkaline sulphydrate and hydrate, to form sulphocarbonates:

$$2KHS \quad + \quad CS_2 \quad = \quad H_2S \quad + \quad K_2CS_3$$
$$6KHO \quad + \quad 3CS_2 \quad = \quad 3H_2O \quad + \quad 2K_2CS_3 \quad + \quad K_2CO_3$$

Its reaction with alcoholic potash, to form the ethyl-oxisulphocarbonate or xanthate of potassium:

$$EtHO \quad + \quad KHO \quad + \quad CS_2 \quad = \quad H_2O \quad + \quad KEtCS_2O$$

Recognition of disulphide of carbon, by formation of black precipitate upon boiling its solution, in aqueous or alcoholic potash, with acetate of lead.

Production of sulphocyanate of ammonia, by reaction at a moderate heat of disulphide of carbon and alcoholic or aqueous ammonia:

$$H_3N \quad + \quad CS_2 \quad = \quad H_2S \quad + \quad HCNS$$

Sulphocarbonic acid, H_2CS_3; obtained as a reddish-brown, oily layer, by decomposing crystalline sulphocarbonate of ammonia with aqueous hydrochloric acid. Its gradual decomposition by water, with production of carbonic and sulphydric acids:

$$H_2CS_3 \quad + \quad 3H_2O \quad = \quad H_2CO_3 \quad + \quad 3H_2S$$

Its expulsion of carbonic acid from the alkali carbonates, and precipitation from most heavy metal salts of sulphocarbonates, gradually changing into sulphides.

Sulphocarbonates. The potassium salt K_2CS_3, made by adding excess of disulphide of carbon to solution of potash, and evaporating resultant solution at low temperature out of access of air. Its occurrence in yellow deliquescent hydrated crystals, becoming anhydrous at 80°. The ammonium salt $(NH_4)_2CS_3$, produced by the direct combination of disulphide of carbon with sulphide of ammonium, or of sulphocarbonic acid with ammonia. Its production by addition of one volume of disulphide of carbon to 8 or 10 volumes of saturated alcoholic solution of ammonia, in a closed vessel surrounded by ice-cold water. Reaction permitted so long as feathery crystals continue to form, or until large prismatic crystals of sulphocarbamate appear. Feathery crystals washed with alcohol and ether successively, pressed between filter-paper, and preserved in well stoppered bottle. A very volatile salt, deliquescent on exposure to air, and decomposible by moderately dilute hydrochloric or sulphuric acid without any evolution of sulphuretted hydrogen, but with simple production of sulphocarbonic acid.

Successive conversion of sulphocarbonate into sulphocarbamate and sulphocyanate of ammonia, by heat or solution in ammonia:

$$\begin{aligned} (H_4N)_2CS_3 \quad &= \quad H_4N.C(H_2N)S_2 \quad + \quad H_2S \\ &= \quad H_4N.CNS \quad + \quad 2H_2S \end{aligned}$$

Existence of acid and neutral sulphocarbonic and oxi- and dioxi-sulphocarbonic ethers, having the respective formulæ:

$$\begin{array}{lll} HEtCS_3 & HEtCS_2O & HEtCSO_2 \\ Et_2CS_3 & Et_2CS_2O & Et_2CSO_2 \end{array}$$

The oxi-sulphocarbonic ethers known as xanthates.

CHLOROCARBONIC COMPOUNDS.

Carbonic chloride or phosgene. *Sym.* Cl_2CO; *p. n.* 99. A product of the direct union of chlorine and carbonous oxide gases, under exposure to sunlight, or when in the nascent state. Also of the action of carbonous oxide on heated perchloride of antimony, &c.:

$$Cl_5Sb + CO = Cl_3Sb + Cl_2CO$$

Its production by metamorphosis of various chlorinated ethers, as perchloromethylic formiate, for example:

$$(Cl_3C)ClCO_2 = Cl_4C_2O_2 = 2Cl_2CO$$

A pungent gas, of sp. gr. $49{\cdot}5 = \frac{99}{2}$. Its solubility in water with decomposition:

$$Cl_2CO + 2H_2O = 2HCl + (HO)_2CO$$

Intermediate decomposition unknown in case of water, but observable with alcohol:

$$Cl_2CO + HEtO = HCl + Cl(EtO)CO$$

Its reaction with ammonia to produce carbamide or urea. Intermediate reaction unknown:

$$Cl_2CO + 2H_3N = 2HCl + (H_2N)_2CO$$

Its reaction with various hydrocarbons, as phenene, to produce chlorides of the next higher acids, as benzoic chloride:

$$Cl_2CO + H_6C_6 = ClH + ClH_5C_7O$$

Sulphocarbonic chloride Cl_2CS, a heavy yellow liquid, produced, together with chloride of sulphur, by reaction of perfectly dry chlorine and disulphide of carbon.

Chlorocarbonic ethers produced as above, by action of carbonic chloride on different alcohols, or of perchlorinated ethers on alcohols:

$$Cl_4C_2O_2 \quad + \quad 2HEtO \quad = \quad 2HCl \quad + \quad 2Cl(EtO)CO$$

Their reaction with ammonia to produce carbamic ethers or urethanes:

$$Cl(EtO)CO \quad + \quad 2H_3N \quad = \quad ClH.H_3N \quad + \quad H_2N(EtO)CO$$

CARBONIC AMIDES.

Carbamic acid. *Sym.* H_3NCO_2; *p. n.* 61.—A compound intermediate between carbonic acid H_2CO_3, and carbamide H_4N_2CO. Its representation as hydrate-amide of carbonyl, carbonic acid being the dihydrate, and carbamide the diamide:

$$(HO)_2CO \qquad HO(H_2N)CO \qquad (H_2N)_2CO$$

Its tantamount representation as a compound of tetrad carbon with diad oxygen, and simultaneously with nitrogen and oxygen each partially saturated by hydrogen:

$$\left.\begin{array}{r}H\\H\\C\\H\end{array}\right\}\begin{array}{l}N\\ \\O\\O\end{array} \quad \text{or} \quad \left.\begin{array}{r}H_2\\H(CO)\end{array}\right\}\begin{array}{l}N\\O\end{array}$$

Carbamic acid known only in form of its ammonium salts and ethers, but sulphocarbamic acid an isolable compound.

Carbamate of ammonium $(H_4N)H_2NCO_2$, produced as a white flocculent mass, on admixture of ammonia and carbanhydride gases in any proportions:

$$(H_3N)_2CO_2 \quad = \quad (H_4N)H_2NCO_2 \quad \text{or} \quad \left.\begin{array}{r}H_2\\H_4N(CO)\end{array}\right\}\begin{array}{l}N\\O\end{array}$$

Its reaction with sulphuric anhydride to form sulphamate of ammonium:

$$SO_3 \quad + \quad (H_4N)H_2NCO_2 \quad = \quad CO_2 \quad + \quad (H_4N)H_2NSO_3$$

Gradual conversion of its aqueous solution into one of diammonium carbonate:

$$(H_4N)H_2NCO_2 \quad + \quad H_2O \quad = \quad (H_4N)_2CO_3$$

Its inability to precipitate calcium salts, until after above conversion by absorption of water. First action of carbanhydride upon strong aqueous ammonia to produce carbamate instead of carbonate of ammonium, shown by inability of liquid to precipitate lime salts, until after some time or upon ebullition. Commercial sesqui-carbonate of ammonium a compound of carbamate and acid carbonate:

$$(H_4N)H_2NCO_2.2(H_4N)HCO_3 \quad = \quad 4H_3N.2H_2O.3CO_2$$

Carbamic ethers. Occurrence of the carbamates of methyl, ethyl, and amyl, or urethylane, urethane, and amylurethane respectively, as fusible volatile solids, which concrete after fusion into beautiful crystalline masses, and also crystallise readily from their respective solutions in water and alcohol. Their production by various reactions, most usually by treatment of the respective chloro-carbonic ethers with ammonia:

$$2H_3N \quad + \quad EtClCO_2 \quad = \quad ClH.H_3N \quad + \quad Et(H_2N)CO_2$$

Correlations of carbamide, urethane, and carbonic ether, shown in following equations:

$$\begin{array}{rcccccl} 2H_3N & + & H_2CO_3 & - & 2H_2O & = & \text{Carbamide} \\ \underbrace{H_3N \quad + \quad H_6C_2O} & + & H_2CO_3 & - & 2H_2O & = & \text{Urethane} \\ 2H_6C_2O & + & H_2CO_3 & - & 2H_2O & = & \text{Carbonic ether} \end{array}$$

Urethane, accordingly, the ether of carbamic acid $H(H_2N)CO_2$, and also the amide of carbethylic acid $EtHCO_3$.

Sulphocarbamic acid, H_3NCS_2, thrown down as a heavy reddish oil on adding crystallised sulphocarbamate of ammonium

to dilute hydrochloric or sulphuric acid. Its decomposition of carbonates with effervescence, to produce sulphocarbamates. Its spontaneous decomposition, with production of sulphocyanic acid:

$$\left.\begin{matrix}H_2\\H(CS)\end{matrix}\right\}\begin{matrix}N\\S\end{matrix} \quad \text{or} \quad H_3N.CS_2 \quad = \quad H_2S \quad + \quad HCNS$$

Sulphocarbamate of ammonium, $\left.\begin{matrix}H_2\\H_4N(CS)\end{matrix}\right\}\begin{matrix}N\\S\end{matrix}$, produced in hard prismatic crystals from mixture of disulphide of carbon and alcoholic solution of ammonia, after deposition of feathery crystals of sulphocarbonate. Salt sparingly soluble in alcohol, freely soluble in water, its solution giving, with heavy metal salts, precipitates of unstable metal sulphocarbamates.

Oxysulphocarbamic ether, sulpho-urethane, or xanthamide, produced by reaction of ammonia upon disulpho-carbonic or xanthic ether, just as urethane is produced by action of ammonia on carbonic ether:

$$H.H_2N \quad + \quad Et_2COS_2 \quad = \quad HEtS \quad + \quad Et(H_2N)COS \quad \text{or} \quad \left.\begin{matrix}H_2\\Et(CS)\end{matrix}\right\}\begin{matrix}N\\O\end{matrix}$$

A highly crystalline body, very similar to urethane, decomposed by alkalis into alcohol and a sulphocyanate,—by heat into mercaptan and cyanic or cyanuric acid:

$$\begin{aligned} EtH_2NCOS \quad &= \quad EtHO \quad + \quad HNCS \\ &= \quad EtHS \quad + \quad HNCO \end{aligned}$$

UREA, ETC.

Carbamide, H_4N_2CO or $(H_2N)_2CO$. Compound considered as identical with urea?

a. Production of carbamide or urea, as of amides in general, by reactions of chloride, acid or anhydride, and ether upon ammonia:

$$\begin{aligned} 2H_3N \quad + \quad Cl_2CO \quad &- \quad 2HCl \\ 2H_3N \quad + \quad H_2CO_3 \quad &- \quad 2H_2O \\ 2H_3N \quad + \quad Et_2CO_3 \quad &- \quad 2HEtO \end{aligned}$$

Conversion of oxamide into urea, as of oxalic into carbonic acid, by its treatment with oxide of mercury, peroxide of manganese, &c.:

$$H_2C_2O_4 + O = H_2CO_3 + CO_2$$
$$H_4N_2C_2O_2 + O = H_4N_2CO + CO_2$$

β. Direct combination of ammonia with cyanic acid to form solid cyanate of ammonium. Its metamorphosis by heat into urea. Discovery of transformation of cyanate of ammonium into urea by Wöhler in 1828:

$$H_3N.HNCO = H_4N_2CO$$

Urea usually made by decomposing aqueous sulphate of ammonium with cyanate of potassium or of lead, separating resulting deposit of sulphate of potassium or lead, evaporating liquid to dryness, and extracting residue with alcohol.

Cyanate of ammonium, and consequently urea, also producible by hydrating cyanamide, decomposing sulphocyanate of ammonium with oxide of silver, &c.

γ. Existence of urea in urine. Its recognisability in crystalline state upon mere evaporation of urine. Its precipitation by ether, from alcoholic extract of evaporated urine. Usual production of urea from urine, in state of sparingly soluble nitrate or oxalate. Filtered urine evaporated down to one-fourth or one-sixth its bulk, and syrupy liquid mixed with an equal volume of strong nitric acid. Deposit of nitrate of urea pressed between tiles, recrystallised from water, redissolved in water, and solution neutralised by potash:

$$H_4N_2CO.HNO_3 + KHO = H_4N_2CO + KNO_3 + H_2O$$

Liquid evaporated to dryness, after separation of chief portion of nitre by crystallisation, and residue extracted with alcohol. Or oxalic acid used instead of nitric acid, and resulting oxalate of urea decomposed with chalk:

$$H_4N_2CO.H_2C_2O_4 + CaCO_3 = H_4N_2CO + CaC_2O_4 + H_2CO_3$$

δ. Production of urea by different processes from various

natural ureides such as kreatine, methyluramine, allantoin, alloxan, uric acid, &c. &c.

Interest of urea as the first organic compound produced artificially. Also as the chief constituent of the urine of mammals, and ultimate product of the metamorphosis of their nitrogenous tissues. Its occurrence in all natural and abnormal fluids of the body, in cases of kidney disease.

Urea a white, crystalline, slightly deliquescent solid, very sparingly soluble in ether, moderately soluble in alcohol, and freely soluble in water. Its deposition in long flat prisms from its aqueous, and in rectangular needles from its alcoholic solution. Its cooling saline taste. Its want of action upon test paper. Its direct combination with certain acids to form salts of urea. Its similar direct combination with neutral salts as of sodium, silver, &c. Its curious separation of water from certain hydrated salts, as sulphate of sodium.

Fusion of urea at 120°. Its decomposition at 150° and upwards into various products, including cyanic acid, melanuric acid, and biuret.

Pure aqueous solution of urea scarcely affected by prolonged ebullition. Its decomposition, when heated to 140° in sealed tubes, with absorption of water:

$$H_4N_2CO \quad + \quad 2H_2O \quad = \quad \overbrace{2H_3N \quad + \quad H_2CO_3}$$

Its similar decomposition in contact with vesical mucus, &c., and when boiled with acids or alkalis. Decomposition of urea by hypochlorites or moist chlorine, and by nitrous acid, with liberation of nitrogen:

$$H_2O \quad + \quad H_4N_2CO \quad + \quad 3Cl_2 \quad = \quad 6HCl \quad + \quad N_2 \quad + \quad CO_2$$
$$H_4N_2CO \quad + \quad 2HNO_2 \quad = \quad 3H_2O \quad + \quad 2N_2 \quad + \quad CO_2$$

Reproduction of ammonia and cyanic or cyanuric acid from the hydrochloride and argento-nitrate of urea.

Urea-salts. Products of the direct combination of urea with certain acids and salts.

$H_4N_2CO.\ HNO_3$	$H_4N_2CO.HCl$
$H_4N_2CO.\ NaNO_3.H_2O$	$H_4N_2CO.NaCl$
$H_4N_2CO.\ AgNO_3$	$H_4N_2CO.HgCl_2$
$H_4N_2CO.\ 2AgNO_3$	
$H_4N_2CO.Hg\left\}\begin{matrix}HO\\NO_3\end{matrix}\right.$	$H_4N_2CO.H_2SO_4$
	$H_4N_2CO.H_2C_2O_4$

Compounds of urea with acids, strongly acid bodies, for the most part stable and crystalline, decomposible by alkali carbonates with separation of urea. Its compounds with salts for the most part easily decomposible, and producible only with salts of much the same solubility as urea itself.

The hydrochloride made by passing dry hydrochloric acid gas over urea heated in a water-bath. Its immediate decomposition by water. Its metamorphosis by heat into hydrochloride of ammonia and cyanic or rather cyanuric acid, $H_3N_3C_3O_3$. The sodio-chloride pre-existent in urine, occasionally recognisable in crystalline state on evaporation of urine, obtainable at will by evaporating down mixed aqueous solution of urea and common salt. The mercuro-chloride obtained by evaporating down mixed alcoholic solutions of urea and corrosive sublimate. The nitrate obtained as a semi-solid crystalline mass on mixing nitric acid with evaporated urine. Its purification by recrystallisation from boiling water. Its occurrence in brilliant leaflets composed of modified rhombic prisms. Its sparing solubility in cold water. Its decomposition by heat of 140° into various products. The sodio-nitrate obtained in long prisms on evaporating mixed solutions of urea and soda-nitre. A very permanent salt, not decomposible by excess of water, or by ebullition, or by addition of nitric or oxalic acid. The argento-nitrate deposited in oblique rhombic prisms on mixing concentrated solutions of urea and nitrate of silver. Compound soluble in hot water without alteration; but decomposible, on evaporation of its solution at boiling heat, into ammonia nitrate and silver cyanate:

$$H_4N_2CO.AgNO_3 \quad = \quad AgNCO \quad + \quad H_3N.HNO_3$$

The di-argento-nitrate obtained on evaporating in vacuo solu-

tion of urea with great excess of silver nitrate. The hydrargyro-nitrate made by adding solution of urea to solution of acid mercuric nitrate, until production of slight turbidity, then filtering and setting aside. Its deposition in rectangular plates. Compound decomposed by boiling water into nitrate of urea, and more basic insoluble hydrargyro-nitrate. The sulphate made by decomposing the oxalate with sulphate of calcium. The oxalate precipitated on addition of strong solution of oxalic acid to concentrated urine. Its alleged occurrence in urine after administration of oxalates. Its moderate solubility in hot, and very sparing solubility in cold water. Its crystallisation in long flat prisms. Its capability of uniting with alkali oxalates to form double salts.

Existence of several compounds of urea with metallic oxides. The mercuric compound $H_4N_2CO.2HgO$, thrown down as a white precipitate on adding mercuric nitrate to an alkaline solution of urea. Production of this precipitate the basis of Liebig's process for estimating urea.

Ureides. A class of bodies analogous to amides. Their representation as compounds of urea with alcohols or acids, minus water. Methyl-urea formed by action of cyanic acid on methylamine, or of methyl cyanate upon ammonia. A substance very similar to urea, decomposible by absorption of water into carbonic acid, methylamine, and ammonia. α-Dimethyl urea made by action of cyanate of methyl upon methylamine, or by some equivalent process. Its decomposition, with absorption of water, into carbonic acid and two atoms of methylamine. Ethyl and α-diethyl urea similar to the above compounds in properties and modes of formation. β-Diethyl urea made by action of cyanic acid upon diethylamine. Its decomposition with absorption of water into carbonic acid, diethylamine, and ammonia.

Formyl-urea at present unknown. Acetyl-urea a neutral body produced, with elimination of hydrochloric acid, by action of acetic chloride upon urea. Its decomposition by heat into cyanic or cyanuric acid and acetamide. Existence of many other

neutral ureides, as butyryl-urea, benzoyl-urea, &c., formed from chlorides of monobasic acids.

Acid ureides, or ureic acids, similarly related to polybasic acids. Composition of carbureic, oxalureic, and mesoxalureic acids:

$$\begin{array}{lclclcl} H_4N_2C_2O_3 & = & H_4N_2CO & + & H_2CO_3 & - & H_2O \\ H_4N_2C_3O_4 & = & H_4N_2CO & + & H_2C_2O_4 & - & H_2O \\ H_4N_2C_4O_5 & = & H_4N_2CO & + & H_2C_3O_5 & - & H_2O \end{array}$$

Mesoxalureic, better known as alloxanic acid, producible by oxidation of uric acid. Oxalureic, or oxaluric acid, occasionally pre-existent in urine as oxalurate of calcium, and producible also by oxidation of uric acid. Carbureic, or allophanic acid, known only in the form of its salts and ethers. Allophanic ether made by condensing cyanic acid vapour in absolute alcohol. A highly crystalline volatilisable body, reacting with caustic alkalis to produce allophanates, as unstable salts, decomposible by ebullition with water into carbonates and urea:

$$NaH_3\ {}_2C_2O_3 \quad + \quad H_2O \quad = \quad H_4N_2CO \quad + \quad NaHCO_3$$

Guanidine, or uramine, H_5N_3C; an alkaloid closely related to carbamic acid and urea. Reaction of the three bodies with water, to form carbonic acid and ammonia:

$$\begin{array}{lclclcl} H_3NCO_2 & = & H_3N & + & H_2CO_3 & - & H_2O \\ H_4N_2CO & = & 2H_3N & + & H_2CO_3 & - & 2H_2O \\ H_5N_3C & = & 3H_3N & + & H_2CO_3 & - & 3H_2O \end{array}$$

Guanidine usually formed by oxidation, with chlorate of potassium and hydrochloric acid, of guanine, an alkaloid extracted from guano, &c.; but also producible by decomposition of biuret; by reaction of chloropicrin with ammonia, &c.:

$$3H_3N \text{ or } H_9N_3 \quad + \quad Cl_3(NO_2)C \quad = \quad H_5N_3C \quad + \quad 3HCl \quad + \quad HNO_2$$

A crystalline, deliquescent, strongly alkaline body, forming well defined crystalline salts, including the carbonate produced by absorption of carbonic acid from the air. Existence of methylguanidine or methyluramine, of triethyluramine, of triphenyluramine, and of diphenyluramine, or melaniline.

Methyluramine, $H_7N_3C_2$, or $(H_3C)H_4N_3C$; produced in the form of oxalate, by oxidation of kreatine with mercuric oxide, &c., and separated from the oxalate by milk of lime:

$$H_9N_3C_4O_2 \quad + \quad O_2 \quad = \quad H_2C_2O_4 . H_7N_3C_2$$

A strongly alkaline, caustic, deliquescent solid, liberating ammonia from sal-ammoniac at ordinary temperatures, forming crystallisable salts, and absorbing carbonic acid from the atmosphere. Its reaction with water, under the influence of alkali, to yield carbonic acid and ammonia plus methylamine:

$$H_7N_3C_2 \quad = \quad \begin{cases} 2H_3N \\ 1H_5NC \end{cases} \quad + \quad H_2CO_3 \quad - \quad 3H_2O$$

Biuret, $H_5N_3C_2O_2$; a product of the decomposition of urea, by prolonged moderate heating. A neutral, stable, crystalline body, soluble in water and alcohol. Manifestation of red colour by reaction of its solutions with a copper salt and alkali. Its conversion into guanidine by treatment with hydrochloric acid, and into cyanuric acid by action of heat. Relationship of urea to biuret and cyanuric acid:

$$\begin{array}{lcccl} 2H_4N_2CO & - & H_3N & = & H_5N_3C_2O_2 \\ 3H_4N_2CO & - & 3H_3N & = & H_3N_3C_3O_3 \end{array}$$

Relationship of allophanic acid and biuret to urea and guanidine respectively:

$$\begin{array}{lcccccl} H_4N_2C_2O_3 & + & H_2O & = & H_4N_2CO & + & H_2CO_3 \\ H_5N_3C_2O_2 & + & H_2O & = & H_5N_3C & + & H_2CO. \end{array}$$

(53.) Cyanogen Compounds.

Similar relationship of prussic acid to marsh-gas and formic aldehyd, and of cyanic acid to methyl alcohol and formic acid:

H_4C	Marsh-gas	$(HO)H_3C$	Methyl alcohol
H_2CO	Form-aldehyd	$(HO)HCO$	Formic acid
HCN	Prussic acid	$(HO)CN$	Cyanic acid

Frequent representation of cyanogen CN, by contracted symbol Cy. Prussic or hydrocyanic acid, HCN or HCy, comparable with hydrochloric acid HCl. Resemblance of cyanogen, C_2N_2 or Cy_2, in several points of its behaviour, to chlorine Cl_2. Marked parallelism in constitution, and frequently in properties and modes of production, of corresponding cyanogen and chlorine compounds:

AuCl,	ClCl,	KCl,	KClO,	HCl,	AgCl,	$HgCl_2$,
AuCy,	CyCy,	KCy,	KCyO,	HCy,	AgCy,	$HgCy_2$.

Production of cyanogen and chlorine gases, by heating cyanide and chloride of gold respectively. Direct combination of cyanogen and chlorine with potassium, to form cyanide and chloride of potassium respectively, as isomorphous soluble salts. Reaction of cyanogen and chlorine with potash, to form mixed cyanide and cyanate, and mixed chloride and hypochlorite of potassium respectively. Decomposition of cyanide and chloride of potassium by sulphuric acid, to liberate hydrocyanic and hydrochloric acids, respectively. Action of nitrate of silver upon the two acids to throw down clotty white precipitates of cyanide and chloride of silver respectively, both of them insoluble in nitric acid and soluble in ammonia. Solubility of oxide of mercury in each of the two acids, to form cyanide and chloride of mercury respectively, as similar crystalline salts. Further correspondence of hydrocyanic ether, cyanacetic acid, iodide of cyanogen, chloride of cyanogen, &c. to hydrochloric ether, chloracetic acid, iodide of chlorine, chloride of chlorine, &c. Consequent consideration of cyanogen compounds as bodies containing a haloid radical analogous to chlorine, and, like chlorine, transferable from one group to another by way of double decomposition.

Marked difference between cyanogen and chlorine in power of combining with other molecules. Union of hydrocyanic acid HCN, as of ammonia H_3N, and of various cyanogen compounds, as of various amidogen compounds, with hydrochloric acid, for example.

Absolute difference between cyanogen and chlorine as respects the tendency of cyanogen to become polymerised, and its capability of undergoing decomposition and recomposition.

Existence of two distinct polymeric cyanogens, of two distinct polymeric cyanic chlorides, and of four distinct polymeric cyanic acids or hydrates, &c.:

$HCNO$	Cyanic acid
$H_3C_3N_3O_3$	Cyanuric acid
$H_6C_6N_6O_6$	Cyanilic acid
$H_xC_xN_xO_x$	Cyamelide

Cyanuren or tricyanogen, the most stable of the polymeric forms of cyanogen. Its formation of a definite chloride, hydrate, amide, &c., corresponding to cyanic chloride, hydrate, amide, &c.

$CN.Cl$	Cyanic chloride	$C_3N_3.Cl_3$	Cyanuric chloride
$\left.\begin{array}{r}CN\\H\end{array}\right\}O$	Cyanic acid	$\left.\begin{array}{r}C_3N_3\\H_3\end{array}\right\}O_3$	Cyanuric acid
$\left.\begin{array}{r}CN\\H\\H\end{array}\right\}N$	Cyanamide	$\left.\begin{array}{r}C_3N_3\\H_3\\H_3\end{array}\right\}N_3$	Cyanuramide

Consequent consideration of cyanogen compounds as bodies existing in different polymeric forms, for the most part susceptible of mutual metamorphosis.

Decomposition and recomposition of cyanogen CN, into or from ammonia, on the one hand, and some methylic or formio-carbonic compound on the other. Dehydration of formiate of ammonia into prussic acid; and rehydration of prussic acid into formiate of ammonia, for example:

$$H_2CO_2.H_3N \quad - \quad 2H_2O \quad = \quad HCN$$

Equivalency, in composition, of one atom of oxalic acid $H_2C_2O_4$, with two atoms of formic acid minus hydrogen, $2H_2CO_2 - H_2$. Hence similar relationships of oxalate of ammonia to cyanogen and of formiate of ammonia to hydrocyanic acid:

$$H_2C_2O_4(H_3N)_2 \quad - \quad 4H_2O \quad = \quad (CN)_2$$

Consequent consideration of cyanogen compounds in respect to the formation and decomposition of their constituent cyanogen.

Ferrocyanide of potassium $K_4FeCy_6.3Aq$, or hydrated double cyanide of potassium and iron $4KCy.FeCy_2.3Aq$, the commercial source of all other cyanogen compounds. Production from it of cyanide of potassium KCy, by its ignition with carbonate of potassium and charcoal; of cyanate of potassium KCyO, by its ignition with litharge; of prussian blue $2Fe_2Cy_6.3FeCy_2$ or Fe_7Cy_{18}, by its precipitation with a persalt of iron; and of mercuric cyanide $HgCy_2$, by its ebullition with mercuric sulphate.

Cyanogen, C_2N_2 or $(CN)_2$; discovered in 1815 by Gay-Lussac, as the first isolated compound radical. *α.* Its production by heating cyanides of noble or semi-noble metals, as of mercury, silver, gold, &c. Gas usually made by heating cyanide of mercury; or chloride of mercury mixed with either cyanide or ferrocyanide of potassium. Its collection over mercury:

$$Hg(CN)_2 \text{ or } HgCy_2 = Hg + Cy_2$$

Appearance of some cyanogen in polymeric form of para-cyanogen, left as a brown infusible residue. *β.* Cyanogen also made by heating oxalate of ammonium with phosphoric anhydride:

$$H_2C_2O_4.H_6N_2 - 4H_2O = C_2N_2$$

Cyanogen liquefiable by pressure of 4·5 atmospheres at 15°; and of 1 atmosphere at −20·5. Its solidification by more intense cold into a transparent crystalline mass, fusing at −34°. Liquid cyanogen obtainable by decomposing mercuric cyanide in sealed Λ-tube. A colourless, refractive liquid, of sp. gr. 0·866, and boiling point −20·5. Gaseous cyanogen a colourless gas of peculiar odour, and sp. gr. $26, = \frac{24+28}{2}$. Solubility of 4·5 volumes of cyanogen gas in one volume of water, and of 23 volumes of the gas in one volume of alcohol. Speedy decomposition of the aqueous solution into various products, including some re-formed oxalate of ammonia, a brown substance known as azulmic acid $C_2N_2.H_2O$, and urea:

$$C_2N_2 + 4H_2O = H_2C_2O_4.H_6N_2$$

Urea probably formed by metamorphosis of cyanic acid (*q. v.*), itself produced by similar action of water as of alkali upon cyanogen:

$$C_2N_2 + H_2O = HCN + HCNO$$
$$C_2N_2 + K_2O = KCN + KCNO$$

Decomposition of cyanogen at a red heat into carbon and nitrogen, especially in presence of iron to take up the carbon. Its combustion in air or oxygen with beautiful rose-red flame. Result of its explosion with oxygen:

$$C_2N_2 + O_4 = C_2O_4 + N_2$$

Its non-combination with oxygen, sulphur, hydrogen, or chlorine. Its combination with sulphuretted hydrogen to form compounds $C_2N_2.H_2S$ and $C_2N_2.2H_2S$. Its combination with heated potassium and sodium to form cyanides of the two metals respectively. Other direct combinations of cyanogen; as with aniline to form cyananiline, with melaniline to form cyanmelaniline, &c.

Paracyanogen C_xN_x, a brown, infusible, insoluble mass, polymeric with cyanogen; produced by the action of heat on cyanide of mercury, and in other ways. Its conversion, by ignition in a current of nitrogen, into cyanogen. Its attackability by chlorine and the alkali metals.

(54.) Hydrocyanic acid and Cyanides.

Circumstances under which cyanides are produced. By decomposition of chloroform with ammonia, especially in presence of potash:

$$H_3N + Cl_3HC = 3HCl + HCN$$

By dry distillation of ammonia-formiate, or formiamide:

$$\left.\begin{array}{ll} & H_3N.(HO)HCO - 2H_2O \\ \text{and} & (H_2N)HCO - H_2O \end{array}\right\} = HCN$$

In small quantity, by passage of ammonia over ignited carbon:

$$2H_3N + C = H_3N.HCN + H_2$$

By passage of ammonia, or even of nitrogen, over ignited carbon and either baryta or carbonate of potassium:

$$N_2 + C_4 + K_2CO_3 = 2KCN + 3CO$$

By ignition of carbo-nitrogenous bodies with preformed potassium or sodium. Reaction used as a test for the presence of nitrogen. On large scale, refuse animal matter ignited with carbonate of potassium in presence of iron. Resulting reduced potassium of the carbonate thereby transformed into cyanide KCN. Crude salt purified by lixiviation, and action of the solution on iron to form the easily crystallisable hydrated double cyanide of potassium and iron $K_4\overset{''}{Fe}Cy_6.3Aq$, known also as ferrocyanide of potassium and familiarly as yellow prussiate of potash.

Production of aqueous hydrocyanic acid by action of water on various seeds, leaves, &c., and its consequent presence in bitter almond oil, cherry laurel water, &c.

Hydrocyanic, or prussic acid, HCN; procurable in anhydrous state by transmission of dried sulphuretted hydrogen over excess of powdered and gently warmed mercuric cyanide:

$$\overset{''}{Hg}(CN)_2 + H_2S = 2HCN + \overset{''}{Hg}S$$

Or by action of sulphuric acid on solution of Wöhler's cyanide of potassium:

$$KCN + H_2SO_4 = HCN + KHSO_4$$

Gas passed over chloride of calcium, and condensed in freezing mixture of ice and salt.

The pure acid a colourless liquid, of sp. gr. 0·6967; solidifiable in freezing mixture of ice and salt; boiling at 26·5°. Vapour density $\frac{1+12+14}{2}=13{\cdot}5$. Rapid vaporisation of acid at ordinary temperatures, with absorption of so much heat, as to effect congelation of unevaporated residue. Decomposition of its vapour by potassium, with formation of potassium cyanide and hydrogen. Combustibility of vapour in air, with pale cyanogen-like flame. Its violent explosion with oxygen:

$$2HCN + O_5 = H_2O + 2CO_2 + N_2$$

Aqueous hydrocyanic acid made by various processes; very readily, and of definite strength, by agitating cyanide of silver in dilute hydrochloric acid; but most usually by action of sulphuric acid on solution of potassium ferrocyanide:

$$2K_4F\overset{''}{e}Cy_6 + 6H_2SO_4 = 6HCy + K_2F\overset{''}{e}_2Cy_6 + 6KHSO_4$$

Expulsion of one moiety of cyanogen of salt as hydrocyanic acid, the other moiety remaining as white ferrocyanide of potassium and iron.

Presence of 2 per cent of anhydrous acid in dilute acid of the Pharmacopœia. Spontaneous weakening even of this dilute solution under exposure to air, by volatilisation from it of hydrocyanic acid vapour; and rapid weakening of more concentrated acid. Peculiar odour and irritating effect on the fauces of hydrocyanic acid vapour, even when very diluted. Intensely toxic character of the acid, both strong and dilute. Speedy decomposition of anhydrous acid into ill-defined brown products, most quickly on exposure to light. Greater stability of aqueous acid, in proportion to its dilution. Its gradual decomposition, however, on exposure to light, with formation of various products, including formiate of ammonia. Its stability increased by slight addition of mineral acid, decreased by addition of alkali. Feebly acid character of hydrocyanic acid. Its expulsion from alkali cyanides, even by carbonic acid of atmosphere. Reaction of acid with caustic potash to form cyanide and formiate successively:

$$HCN + KHO = KCN + H_2O$$
$$HCN + KHO + H_2O = KHCO_2 + H_3N$$

Sudden decomposition of concentrated acid by excess of hydrochloric acid, into formic acid and ammonia:

$$HCN + 2H_2O + HCl = H_2CO_2 + H_3N.HCl$$

Action of nascent hydrogen on hydrocyanic acid to furnish methylamine:

$$HCN + H_4 = H_5CN$$

Action of chlorine to produce cyanic or cyanuric chloride, and intermediate hydrochloride:

$$HCN + Cl_2 = Cl\,C\,N + HCl$$
$$3HCN + 3Cl_2 = Cl_3C_3N_3 + 3HCl$$
$$3HCN + 2Cl_2 = HCl_2C_3N_3 + 2HCl$$

Direct combination of hydrocyanic acid with hydracids, metallic chlorides, &c. after the fashion of ammonia; and with various unsaturated organic bodies, after the fashion of hydrogen, hydrochloric acid, and chlorine.

Tests for hydrocyanic acid in mixtures, based on reactions of spontaneously evolved vapour—with silver nitrate to form opaque white silver cyanide; with ammonium persulphide to form ammonium sulphocyanate, convertible into blood-red ferric sulphocyanate on addition of ferric salt; and with mixed potash and iron sulphate to form potassium ferrocyanide, convertible into dark blue ferric ferrocyanide, or prussian blue, on addition of hydrochloric acid. Effect of hydrochloric acid to dissolve up excess of iron oxides, and so form ferric chloride to react with the potassium ferrocyanide:

$$HCN + AgNO_3 = AgCN + HNO_3$$
$$HCN + (NH_4)_2S_2 = NH_4CNS + NH_4HS$$
$$6HCN + 4KHO + FeO = K_4Fe(CN)_6 + 5H_2O$$

Cyanide of potassium, KCN. Liebig's, or the commercial salt, made by igniting mixture of dried ferrocyanide and carbonate of potassium:

$$K_4FeCy_6 + K_2O.CO_2 = 5KCy + KCyO + Fe + CO_2$$

Fused mixture of cyanide and cyanate poured away from reduced iron, and after solidification broken in pieces. Its occurrence in opaque, white, irregular masses. Wöhler's, or pure cyanide of potassium, made by igniting above mixture with excess of charcoal:

$$K_4FeCy_6 + K_2O.CO_2 + C_2 = 6KCy + Fe + 3CO$$

Fused mass exhausted with water in closed vessels, and solution used or evaporated down.

Deliquescence in moist air, and extreme solubility in water of potassium cyanide. Its moderate solubility in hot alcohol, and separation therefrom, on cooling, in cubical crystals resembling those of the chloride. Its alkaline reaction; and evolution, on exposure to air, of hydrocyanic acid. Its use as a reducing flux.

Solubility of cyanides of alkali- and alkaline-earth metals, magnesium, and mercury. Insolubility of most other cyanides. Their production by precipitation of heavy metal salts with cyanide of potassium:

$$2KCy + NiCl_2 = 2KCl + NiCy_2$$

Precipitates soluble in excess of aqueous potassium cyanide, with formation of double crystallisable compounds, not decomposible by excess of potash, such as $AgCy.KCy$, $AuCy.KCy$, $NiCy_2.2KCy$, $ZnCy_2.2KCy$, &c. Precipitation of these double cyanides of alkali metal by salts of heavy metal:

$$NiCy_2.2KCy + Pb(NO_3)_2 = NiCy_2.PbCy_2 + 2KNO_3$$
$$NiCy_2.2KCy + NiCl_2 = 2NiCy_2 + 2KCl$$

Precipitation also of above alkali double cyanide solutions by dilute acids, with liberation of hydrocyanic acid:

$$NiCy_2.2KCy + 2H_2SO_4 = NiCy_2 + 2HCy + 2KHSO_4$$

Decomposition of precipitated insoluble cyanides by stronger mineral acids, either in the cold or upon boiling:

$$NiCy_2 + 2HCl = 2HCy + NiCl_2$$

Solubility of zinc, iron, &c., in heated cyanide of potassium solution, with formation of double cyanide, and liberation of hydrogen:

$$4KCy + Zn + 2H_2O = ZnCy_2.2KCy + 2KHO + H_2$$

Solubility of most metals, including silver and gold, in cyanide of potassium solution, with absorption of oxygen:

$$4KCy + Au_2 + H_2O + O = 2(AuCy.KCy) + 2KHO$$

Cyanide of silver, AgCy; a white clotty precipitate resembling

the chloride, soluble in ammonia, insoluble in cold, but soluble in boiling concentrated nitric acid; and decomposible by hydrochloric, with evolution of hydrocyanic acid. Its decomposition by heat, with evolution of cyanogen. Its solubility in cyanide of potassium solution, to form double salt AgCy.KCy, crystallising in anhydrous octahedrons or hexagonal plates. Silver of double salt not precipitable by soluble hydrates or chlorides, save hydrochloric acid. Estimation of strength of hydrocyanic acid by supersaturating it with potash, and then adding standard solution of nitrate of silver until occurrence of precipitate, through conversion of more than half of produced alkali cyanide into cyanide of silver:

$$2KCy + AgNO_3 = KCy.AgCy + KNO_3$$

Use of above double salt in plating and electroplating. Its occasional production in photographic processes.

Cyanide of gold, AuCy; a lemon-yellow crystalline precipitate, thrown down from auric chloride $AuCl_3$, by cyanide of potassium. Its insolubility in acids, except boiling *aqua regia*. Its decomposition by heat into cyanogen and gold. Its solubility in cyanide of potassium to form double salt AuCy.KCy, crystallising in colourless scales or octahedrons. Use of double salt in plating and electroplating.

Cyanide of mercury, $HgCy_2$; made by boiling prussian blue, or saturating cyanide of hydrogen or ammonium, with mercuric oxide:

$$Fe_7Cy_{18} + 9HgO = 9HgCy_2 + Fe_7O_9$$

Also by boiling mercuric sulphate or nitrate with ferrocyanide of potassium:

$$K_4FeCy_6 + 3HgSO_4 = 3HgCy_2 + 2K_2SO_4 + FeSO_4$$

An anhydrous salt, almost insoluble in alcohol, soluble in eight parts of cold, freely soluble in hot water, and crystallising therefrom in opaque white prisms. Its decomposition by heat into mercury and cyanogen, with some paracyanogen. Non-precipitability of its solution by alkalis. Its formation of various

double salts, such as the iodocyanide HgCyI. Its decomposition by heated sulphuric or hydrochloric acid, with formation of hydrocyanic acid; and by aqueous chlorine, with formation of chloride of cyanogen.

FERROCYANIDES, ETC.

Existence of more stable class of double cyanides, differing from those above described in being non-poisonous and non-precipitable by acidification, and in yielding corresponding hydrogen salts or acids. Ferrocyanide of potassium, $4KCy.FeCy_2$ or $K_4\overset{''}{F}eCy_6$, corresponding to hydroferrocyanic acid $H_4\overset{''}{F}eCy_6$, the type of stable class of double cyanides. Intimate association of its entire cyanogen with iron, to form the tetrad compound radical $\overset{''}{F}eCy_6$, or ferrocyanogen. (?) Existence of its cyanogen in polymeric form of tricyanogen or cyanuren. (?) Non-recognisability of irôn in ferrocyanides by ordinary reagents, including sulphide of ammonium. But production of iron in easily recognisable form by various decompositions of ferrocyanides, as by boiling potassium salt with sulphate of hydrogen or of mercury, boiling ferric salt (prussian blue) with oxide of mercury, &c. In electrolysis of ferrocyanide solutions, iron liberated, together with hydrocyanic acid, at positive, and alkali alone at negative pole.

Hydroferrocyanic acid, H_4FeCy_6; producible by decomposition of potassium ferrocyanide with tartaric acid; best made by adding ether and then hydrochloric acid to cold saturated solution of potassium ferrocyanide in air-free water. Resulting white scales of hydroferrocyanic acid washed with mixed alcohol and ether, and dried over oil of vitriol in vacuo. A tetrabasic acid, soluble in water and alcohol, and precipitable from its alcoholic solution on addition of ether. Its oxidation on exposure to air, with production of some form of prussian blue. Decomposition of its solution when boiled, with evolution of hydrocyanic acid, and deposition of white ferrous cyanide $FeCy_2$, convertible on exposure to air into a form of prussian blue.

Potassium ferrocyanide, $K_4FeCy_6.3Aq$; producible by allowing aqueous potassium cyanide to act on metallic iron or on ferrous oxide or sulphide:

$$6KCy + 2H_2O + Fe = K_4FeCy_6 + 2KHO + H_2$$
$$6KCy + H_2O + FeS = K_4FeCy_6 + KHO + KHS$$

Made on large scale, in nearly pure state, by heating refuse animal matter, such as horn and hoof parings, hide and leather clippings, dried blood, &c., with carbonate of potassium and iron filings, in covered iron pots, lixiviating fused mass, and crystallising resultant solution. Ferrocyanide produced during lixiviation, by action of already formed potassium cyanide on remaining iron, and on ferrous sulphide formed by union of some iron with sulphur furnished by animal matter and by sulphate of potassium existing as impurity in the carbonate. Salt also producible by various reactions.

Ferrocyanide of potassium a pale amber-yellow salt, occurring in large tabular crystals, cleavable into laminæ, and very tough. Its dehydration at 100°, fusion at a red heat in closed vessels, and gradual decomposition at strong red heat into cyanide of potassium, carbide of iron, and nitrogen. Its solubility in four parts of cold, and two of boiling water, insolubility in alcohol, and sparing solubility in strong solution of potash. Its saline somewhat bitter taste, and want of poisonous character. Gradual assumption of blue colour by its acidified solution, through oxidation of liberated hydroferrocyanic acid. Decomposition of its solution, when distilled with sulphuric acid, to yield hydrocyanic acid, and ferrocyanide of iron and potassium $K_2\overset{''}{Fe}(\overset{''}{Fe}Cy_6)$. Its decomposition by concentrated sulphuric acid with evolution of carbonous oxide. Its conversion into cyanide of potassium by ignition with carbonate of potassium, or mixed carbonate of potassium and charcoal. Its conversion into cyanate of potassium KCyO, by ignition with oxide of lead, peroxide of manganese &c.; and into sulphocyanate KCyS, by ignition with sulphur. Its conversion into ferridcyanide of potassium $K_3\overset{'''}{Fe}Cy_6$, by chlorine and most other oxygenants acting at ordinary temperatures. Its

conversion into nitroprusside of potassium $(K_2\overset{iv}{Fe}Cy_5)_2N_2O_3$, by moderately strong nitric acid; and complete decomposition by the boiling concentrated acid.

Reaction of ferrocyanide of potassium with solutions of most metallic salts to throw down precipitates, consisting of ferrocyanide of heavy metal, as $\overset{''}{Cu}_2(\overset{iv}{Fe}Cy_6)$; or, with the ferrocyanide in excess, of double ferrocyanide of heavy metal and potassium, as $K_2\overset{''}{Cu}(\overset{iv}{Fe}Cy_6)$. Precipitates of manganese and cadmium soluble in dilute hydrochloric acid, the rest insoluble. Precipitation of iron, blue (pure ferrous salt white); of cobalt, lavender; of nickel, pale green; of copper and uranium, chocolate-red; and of other precipitable metals, white.

Action of chlorine on ferrocyanide of potassium to abstract one-fourth of potassium, and so leave iron in the state of triad ferricum instead of diad ferrosum, with production of ferridcyanide of potassium or red prussiate of potash:

$$2K_4(\overset{iv}{Fe}Cy_6) \quad + \quad Cl_2 \quad = \quad 2KCl \quad + \quad 2K_3(\overset{'''}{Fe}Cy_6)$$

Ferridcyanogen considered as a radical analogous to ferrocyanogen, usually as a triad, by formula $\overset{'''}{Fe}Cy_6$; but by some authors, as a hexad, by formula $\overset{vi}{Fe}_2Cy_{12}$.

Hydroferridcyanic acid, $H_3(\overset{'''}{Fe}Cy_6)$ or $H_6(\overset{vi}{Fe}_2Cy_{12})$, produced in brown, deliquescent needles, by treating cold saturated solution of ferridcyanide of potassium with large excess of concentrated hydrochloric acid; or suspended ferridcyanide of lead with dilute sulphuric acid.

Ferridcyanide of potassium, $K_3(\overset{'''}{Fe}Cy_6)$ or $K_6(\overset{vi}{Fe}_2Cy_{12})$, usually made by exposing powdered ferrocyanide of potassium to chlorine gas; or by passing the gas through solution of ferrocyanide until it ceases to give blue precipitate with ferric chloride. Separation of resulting ferridcyanide from chloride of potassium by crystallisation. Salt often contaminated with ill-defined green compound, produced by excess of chlorine, and very difficult to remove. Pure salt obtainable by other processes (*vide infra*). Occurrence of ferridcyanide of potassium in fine garnet-red, an-

hydrous, prismatic crystals, soluble in $2\frac{1}{2}$ parts of cold and less than $1\frac{1}{2}$ parts of boiling water, to form a brown or greenish brown solution. Decomposibility of the salt by heat, and its combustibility in air with scintillation. Its conversion into nitroprusside by nitrous or nitric acid, and into ferrocyanide by reducing agents, as sodium amalgam. Use of ferridcyanide of potassium, especially in presence of alkali, as an oxidising agent, to produce peroxide of lead for instance:

$$PbO + 2KHO + 2K_3(\overset{\prime\prime\prime}{Fe}Cy_6) = PbO_2 + H_2O + 2K_4(\overset{\prime\prime}{Fe}Cy_6)$$

Its employment as an oxygenant in calico-printing, to discharge the colour of indigo.

Ordinary prussian blue, or ferric ferrocyanide, $\overset{\prime\prime\prime}{Fe}_4(\overset{\prime\prime}{Fe}Cy_6)_3$ or Fe_7Cy_{18}; usually made by adding ferrocyanide of potassium, or preferably hydroferrocyanic acid, to excess of ferric chloride. Deep blue velvety precipitate, drying up into compact mass, assumptive of coppery lustre by friction. Insolubility of precipitate in mineral acids; its solubility in oxalic acid, and production in state of watery solution by dialysing away oxalic acid. Its decomposition by potash, with reproduction of potassium ferrocyanide and ferric oxide. Its decomposition by mercuric oxide, with production of mercuric cyanide and ferric oxide. Its complete decomposition when boiled with strong mineral acids, and when treated with chlorine.

Soluble prussian blue, or potassio-ferric ferrocyanide, $K\overset{\prime\prime\prime}{Fe}(\overset{\prime\prime}{Fe}Cy_6)$; thrown down as a deep blue precipitate on adding ferric chloride to excess of potassium ferrocyanide. Its insolubility in saline solutions, but solubility in pure water. Its isomerism with Williamson's prussian blue. Its decomposition by potash, with formation of ferric oxide.

Everitt's salt, or potassio-ferrous ferrocyanide, $K_2\overset{\prime\prime}{Fe}(\overset{\prime\prime}{Fe}Cy_6)$; a white, usually somewhat bluish, compound, formed in manufacture of prussic acid by action of sulphuric acid on ferrocyanide of potassium. Its probable identity with white precipitate formed

by adding pure ferrous sulphate to ferrocyanide of potassium. Its conversion by exposure to air into basic prussian blue.

Basic prussian blue, or oxiferrocyanide, $\overset{'''}{Fe}_2\left\{\begin{matrix}O\\ Fe''Cy_6\end{matrix}\right.$ or Fe_3Cy_6O $= \frac{1}{3}\{\overset{'''}{Fe}_4(\overset{''}{Fe}Cy_6)_3.Fe_2O_3\}$, made by exposing above preparation to the air and washing away reproduced ferrocyanide of potassium:

$$2K_2\overset{''}{Fe}(\overset{''}{Fe}Cy_6) + O = K_4(\overset{''}{Fe}Cy_6) + Fe_3Cy_6O$$

Its slight solubility in water; and convertibility into ordinary prussian blue by treatment with strong hydrochloric acid, so as to remove constituent ferric oxide.

Turnbull's blue, or ferrous ferridcyanide, $\overset{''}{Fe}_3(\overset{'''}{Fe}Cy_6)_2$ or Fe_5Cy_{12}; formed by reaction of potassium ferridcyanide and ferrous sulphate. Its decomposition by potash, with formation of ferrocyanide of potassium and magnetic oxide of iron:

$$8KHO + Fe_5Cy_{12} = 2K_4\overset{''}{Fe}Cy_6 + 4H_2O + Fe_3O_4$$

Williamson's prussian blue, or potassio-ferrous ferridcyanide, $K\overset{''}{Fe}(\overset{'''}{Fe}Cy_6)$, made by acting on Everitt's salt with chlorine or nitric acid. Its relation to Everitt's salt precisely that of ferridcyanide to ferrocyanide of potassium. Its isomerism with soluble prussian blue $K\overset{'''}{Fe}(\overset{''}{Fe}Cy_6)$. Its reaction with ferrocyanide of potassium solution, to reproduce Everitt's salt and pure ferridcyanide of potassium:

$$K_4(\overset{''}{Fe}Cy_6) + K\overset{''}{Fe}(\overset{'''}{Fe}Cy_6) = K_2\overset{''}{Fe}(\overset{''}{Fe}Cy_6) + K_3(\overset{'''}{Fe}Cy_6)$$

N i t r o p r u s s i d e s producible by action of nitric acid on ferro- and ferrid-cyanides. Simplest reaction that of nitrous anhydride on a ferridcyanide, with exchange of $\frac{1}{2}N_2O_3$ for $M'Cy$:

$$2K_3FeCy_6 \text{ or } K_6Fe_2Cy_{12} + N_2O_3 = K_4Fe_2Cy_{10}.N_2O_3 + 2KCy$$

Nitroprussic acid, $H_4Fe_2Cy_{10}.N_2O_3.2Aq$; a crystallisable compound, similarly producible from hydroferrocyanic acid. Nitroprusside of sodium $Na_4Fe_2Cy_{10}.N_2O_3.4Aq$, the best known salt, from its ready crystallisation, in garnet-red prisms. Its solubility in $2\frac{1}{2}$ parts of cold water.

Reaction of nitroprussides with soluble sulphydrates and monosulphides, to produce deep purple colour. With polysulphides, colour very evanescent, through production of nitroferrosulphides. Relationship of nitroprussides to nitroferrosulphides, as of

$$Na_4Fe_2Cy_{10}.N_2O_3 \quad \text{to} \;.\;.\;. \begin{cases} Na_6Fe_2S_6N_2O_3 \\ Na_4Fe_2S_5N_2O_3 (?) \\ Na_2Fe_2S_4N_2O_3 \\ \quad Fe_2S_3N_2O_3 \end{cases}$$

Production of nitroprussides by boiling nitroferrosulphides with mercuric cyanide; and of nitroferrosulphides by boiling nitroprussides with alkaline persulphides. Intimate constitution of nitroprussides. (?)

Dissolution of cobaltous cyanide $CoCy_2$, in aqueous cyanide of potassium, to form double cyanide $CoCy_2.2KCy$, decomposible on acidification of solution, with liberation of hydrocyanic acid and reprecipitation of cobaltous cyanide. Production, by exposure to air of cobaltous cyanide dissolved in excess of cyanide of potassium, of the cobalticyanide $K_3\overset{'''}{Co}Cy_6$, analogous to and isormorphous with ferridcyanide of potassium. Its decomposition by hydrochloric acid, with formation of soluble hydrocobalticyanic acid $H_3\overset{'''}{Co}Cy_6$, instead of insoluble cobaltous cyanide:

$$8KCy \;+\; 2CoCy_2 \qquad H_2O \;+\; O \;=\; 2K_3CoCy_6 \;+\; 2KHO$$

Existence of similar chromicyanide of potassium $K_3\overset{'''}{Cr}Cy_6$.

Platinocyanide of potassium $K_2\overset{''}{Pt}Cy_4$, a beautiful dichroic salt, made by dissolving platinous cyanide in cyanide of potassium. Its conversion into colourless platinidchlorocyanide $K_2\overset{''''}{Pt}Cy_4Cl_2$, by action of chlorine. Combination of one atom of this chlorocyanide with five atoms of the platinocyanide, to form complex double salt $K_{12}Pt_6Cy_{24}Cl_2$, formerly known as platinicyanide of potassium. Replacement of its chlorine by other acid radicals, as SO_4, $(NO_3)_2$, &c.

(55.) Cyanic and Cyanuric Compounds.

Existence of cyanogen representatives of hydrochloric acid, water, and ammonia; or cyanic chloride, acid, and amide respectively:

$Cl.H$	$HO.H$	$H_2N.H$
$Cl.CN$	$HO.CN$	$H_2N.CN$

Also of various polymers of these bodies, especially cyanuric chloride, cyanuric acid, and cyanur-amide or melamine:

$$Cl_3.C_3N_3 \qquad (HO)_3.C_3N_3 \qquad (H_2N)_3.C_3N_3$$

Occurrence in cyanuric series, of bodies intermediate between the amide and the acid or chloride, such as melanuric acid $\begin{matrix}(HO)_2\\(H_2N)\end{matrix}.C_3N_3$, chlorocyanuramide $\begin{matrix}Cl\\(H_2N)_2\end{matrix}.C_3N_3$, &c.

CYANOGEN CHLORIDES.

Cyanic chloride, ClCN. Its production in two distinct forms. The gaseous chloride usually made by action of chlorine gas on moistened cyanide of mercury; but also producible from diluted hydrocyanic acid:

$$Hg(CN)_2 \quad + \quad 2Cl_2 \quad = \quad HgCl_2 \quad + \quad 2ClCN$$

A neutral, colourless, excessively pungent gas, liquefying at $-15°$, and solidifying in long needles at $-18°$. Gradual conversion of liquefied gas, preserved in sealed tubes, into cyanuric chloride. Solubility, in one volume of water at $15°$, of 25 volumes of the gas, expelled without change on heating solution. Free solubility of the gas in alcohol and ether. Its reaction with ammonia to form cyanamide, and with fixed alkali to form a cyanate or its products of decomposition.

The liquid chloride made by passing chlorine into moderately concentrated hydrocyanic acid, maintained at 0°:

$$3HCN \quad + \quad 2Cl_2 \quad = \quad HCN.2ClCN \quad + \quad 2HCl$$

Resulting double hydride-chloride produced in form of supernatant layer, washed with ice-cold water, decomposed with excess of mercuric oxide, and product distilled over chloride of calcium.

A mobile liquid, of odour very like that of the gaseous chloride, solidifying at $-5°$, and boiling at $15°$. Its sparing solubility in water, free solubility in alcohol and ether. Its permanence when pure, but speedy conversion into cyanuric chloride if retaining excess of chlorine. Difference between gaseous and liquid cyanic chloride unexplained.

The hydride-chloride, $HCN.2ClCN$ or $HCl_2C_3N_3$, a definite compound, boiling at $20°$, permanent when pure, but, with excess of chlorine, soon changing into cyanuric chloride.

Cyanuric chloride, $Cl_3C_3N_3$; produced as above described, by metamorphosis of cyanic chlorides; also by acting on dry hydrocyanic acid or mercuric cyanide with chlorine, under exposure to sunlight; and as a product of the action of phosphorus pentachloride on cyanuric acid.

White needles or plates, of sp. gr. 1·3, melting at $140°$, boiling at $190°$, and having a characteristic pungent odour. Free solubility of cyanuric chloride in alcohol and ether. Its sparing solubility in water. Decomposition of its solution in water and alcohol, into cyanuric and hydrochloric acids. Its reaction with ammonia, to produce chlorocyanuramide:

$$Cl_3.C_3N_3 \quad + \quad 3H_2O \quad = \quad (HO)_3.C_3N_3 \quad + \quad 3HCl$$
$$Cl_3.C_3N_3 \quad + \quad 2H_3N \quad = \quad Cl(H_2N)_2.C_3N_3 \quad + \quad 2HCl$$

CYANOGEN HYDRATES.

Great instability of cyanic acid and of its soluble salts, in presence of water. Conversion of aqueous cyanate of ammonia into urea:

$$H_3N.HCNO \quad = \quad H_4N_2CO \quad \text{or} \quad (H_2N)_2CO$$

Conversion of aqueous cyanate of potassium into ammonia and acid-carbonate of potassium:

$$KCNO \quad + \quad 2H_2O \quad = \quad H_3N \quad + \quad KHCO_3$$

Conversion of aqueous cyanic acid, chiefly into acid-carbonate of ammonia, partly into urea:

$$HCNO + 2H_2O = H_3N.H_2CO_3$$
$$HCNO + H_3N = H_4N_2CO$$

Cyanates, except cyanate of ammonia, tolerably permanent in dry state. But speedy change of dry cyanic acid into solid mass of cyamelide. Liberation, by acting on cyanates with stronger acids, of cyanic acid—quickly transformed, in presence of water, into acid-carbonate of ammonia, and in absence of water, into cyamelide.

Cyanic acid, $HCNO$; always made by distilling cyanuric acid $H_3C_3N_3O_3$, and condensing product at or below 0°; or reproduced by distilling cyamelide. A mobile, strongly vesicating liquid, evolving pungent irritant vapours. Its spontaneous and rather sudden change, after some hours, with great evolution of heat, into a porcellanous mass of cyamelide. Its reaction with water to form ammonia acid-carbonate and urea (*vide supra*). Its reaction with alcohol to form carbureic ether (allophanic ether):

$$H(H_5C_2)O + 2HCNO = (H_5C_2)H_3N_2C_2O_3 \text{ or } H_5C_2(H_3N_2CO)CO_2$$

Cyanates. That of potassium $KCNO$, the best known. Formed under various circumstances, as in deflagration of carbon and carbonaceous substances with nitre; by ignition of cyanuric compounds with caustic potash; and, together with cyanide or chloride, by action of cyanogen or chloride of cyanogen on caustic potash:

$$(CN)_2 + 2KHO = KCN + KCNO + H_2O$$
$$ClCN + 2KHO = KCl + KCNO + H_2O$$

Salt always made by direct oxidation of the cyanide. Ferrocyanide of potassium heated under exposure to air, or in admixture with peroxide of manganese. Preferably, cyanide of potassium heated with litharge:

$$KCN + PbO = KCNO + Pb$$

A fusible mass, soluble in and crystallisable from alcohol, easily

soluble in water. Gradual decomposition of the salt, in moist state or in aqueous solution, into acid-carbonate of potassium and ammonia. Action of hydrochloric or diluted sulphuric acid upon the cyanate to set free a little cyanic acid, but to convert the greater part into carbonic acid and ammonia. Action of acetic acid, or deficit of mineral acid, to produce potassium cyanurate:

$$3KCNO \quad + \quad 2H_4C_2O_2 \quad = \quad KH_2C_3N_3O_3 \quad + \quad 2KH_3C_2O_2$$

Action of crystallised oxalic acid to set free cyanic acid, in form of cyamelide. Cyanate reconverted into cyanide of potassium by ignition with charcoal.

Ammonia cyanate, $H_3N.HCNO$; made, in solid form, by combination of cyanic acid and ammonia vapours. Salt changed into urea; in dry state by fusion; in solution, spontaneously, but more rapidly on application of heat. After transformation, smell of ammonia no longer manifested on addition of fixed alkali, or smell of cyanic acid on addition of sulphuric acid. In artificial production of urea, cyanate of potassium or lead decomposed by sulphate of ammonia, and resulting solution of cyanate of ammonia or urea evaporated down. Cyanate of ammonia also formed by decomposition of cyanate of silver with solution of sal-ammoniac.

Cyanate of lead, $Pb(CNO)_2$; producible as a white crystalline precipitate on decomposing crude cyanate of potassium solution with acetate of lead.

Cyanate of silver, AgCNO; producible as an amorphous white precipitate by double decomposition; and, together with nitrate of ammonia, by evaporating down argento-nitrate of urea:

$$H_4N_2CO.AgNO_3 \quad = \quad H_3N.HNO_3 \quad + \quad AgCNO$$

Cyanuric acid, $H_3C_3N_3O_3$ or $(HO)_3C_3N_3$. Production by various processes, from urea or anomalous cyanate of ammonia, of cyanuric instead of cyanic acid. Solid greyish residue left upon heating urea, dissolved in concentrated sulphuric acid. After addition of a drop or two of nitric acid to effect decoloration, the whole diluted with water. Cyanuric (pyro-uric) acid deposited

in crystals on cooling. Or hydrochloride of urea heated in current of hydrochloric acid gas. Volatilisation of sal-ammoniac with sudden increase of temperature, to leave cyanuric acid, afterwards purified by crystallisation from hot water:

$$3(H_4N_2CO.HCl) \text{ or } 3(H_3N.HCNO.HCl) = 3(H_3N.HCl) + H_3C_3N_3O_3$$

Or chlorine gas passed over heated urea, with production of free nitrogen, hydrochloric acid, sal-ammoniac, and cyanuric acid, the latter purified by crystallisation from hot water:

$$\left.\begin{matrix}3H_4N_2CO \text{ or}\\ 3(H_3N.HCNO)\end{matrix}\right\} + 3Cl_2 = N_2 + 5HCl + NH_3HCl + H_3C_3N_3O_3$$

Cyanuric acid soluble in boiling water, and in concentrated hydrochloric, nitric, and sulphuric acids, without change. Its sparing solubility in cold water. Its decomposition, by prolonged boiling with water, into carbonic acid and ammonia. Its conversion, by dry distillation, into cyanic acid. Production of cyanate of potassium by its fusion with caustic alkali. Production of cyanuric chloride by its reaction with phosphorus pentachloride. The cyanuric, a tribasic acid. Replacement of its three hydrogen atoms by a feebly basylous metal, as silver; but replacement of two atoms only by a strongly basylous metal, as potassium. Monopotassium cyanurate produced by addition of alkali to cyanuric acid, or by treating cyanate of potassium with acetic acid. Dipotassium cyanurate made by crystallising above salt from, or dissolving cyamelide in excess of, caustic alkali. Tri-silver cyanurate made by addition of nitrate of silver to hot solution of cyanuric acid in excess of ammonia.

Cyanilic acid, $H_6C_6N_6O_6$(?); a crystalline soluble acid, produced by boiling mellon or melam in nitric acid, and converted into cyanuric acid by dissolution in sulphuric acid and precipitation therefrom by water.

Cyamelide, $H_xC_xN_xO_x$; obtained as a solid, white, insoluble mass, by spontaneous metamorphosis of distilled cyanic acid, and also by action of concentrated acids upon cyanate of potassium. Its reconversion, by distillation, into cyanic acid. Its solution in

caustic alkali, with formation of alkali-cyanurate. Its decomposition, by ebullition with sulphuric acid, into carbonic acid and ammonia.

Dicyanic acid, $H_2C_2N_2O_2$; an imperfectly known dibasic acid, formed by decomposing cyanurea with nitrous acid:

$$(CN)H_3N_2CO + HNO_2 = H_2C_2N_2O_2 + N_2 + H_2O$$

CYANOGEN SULPHYDRATES, ETC.

Sulphocyanates producible by various reactions. Conversion of potassium cyanide into sulphocyanate by sulphuration, analogous to its conversion into cyanate by oxidation. Solution of cyanide boiled with sulphur, or dry salt fused with sulphur, or dried ferrocyanide of potassium ignited with carbonate of potassium and sulphur:

$$KCN + S = KCNS$$

Product lixiviated, and solution evaporated down. Sulphocyanate of potassium KCNS, a white, deliquescent, crystalline, nitre-like salt, fusible at a moderate heat, soluble in alcohol, very soluble in water.

Sulphocyanate of ammonium $H_3N.HCNS$ or $(H_4N)CNS$, a very similar salt, producible by decomposing the potassium salt with sulphate of ammonium; but usually made by reaction of ammonia and disulphide of carbon in presence of alcohol:

$$3H_3N + CS_2 = H_3N.HCNS + H_3N.H_2S$$

Its occurrence, by similar reaction, as a product of gas purification. Conversions of sulphocarbonate and sulphocarbamate of ammonia into sulphocyanate, spontaneously, or by heat, or by solution in ammonia—through removal of sulphydric acid:

$H_4N.H_4N.CS_3$	or	$H_8N_2CS_3$	Sulphocarbonate
$H_4N.H_2N\ CS_2$	„	$H_6N_2CS_2$	Sulphocarbamate
$H_4N.N\ CS$	„	H_4N_2CS	Sulphocyanate

Salt also produced from prussic acid, by joint action thereon of ammonia, and of sulphur dissolved in sulphide of ammonium:

$$H_3N + HCN + S = H_4N.CNS$$

Effect of heat on sulphocyanate of ammonium to leave greyish

white pulverulent residue of melam. Intermediate production of sulpho-urea H_4N_2CS.

Solutions of most heavy metals precipitated by soluble sulphocyanates. Mercurous sulphocyanate obtained by precipitation of mercurous nitrate. Its decomposition by heat, with singular intumescence. Ferric salts not precipitated, but blood-red ferric sulphocyanate formed in solution. With excess of ferric salt, red colour of the sulphocyanate not destroyed by acidification or ebullition, but immediately on addition of corrosive sublimate; also by zinc and dilute acid with evolution, as from other sulphocyanates, of sulphuretted hydrogen. Reaction with ferric salts employed as a test for sulphocyanates. Their existence thus shown in saliva of man and sheep, and in decoctions of cruciferous seeds.

Sulphocyanic acid, HCNS; made by decomposing sulphocyanate of mercury with sulphydric or hydrochloric acid gases. Or, in solution, by decomposing sulphocyanate of barium with dilute sulphuric acid, &c. A volatile, sour, pungent, oily liquid, solidifying at $-12{\cdot}5°$ into mass of hexagonal prisms, and boiling at $102{\cdot}5°$. Its aqueous solution somewhat unstable, undergoing a decomposition similar to that of cyanic acid. Its reaction with sulphydric acid strictly analogous to that of cyanic acid with water:

$$HCNO + 2H_2O = NH_3.H_2CO_3$$
$$HCNS + 2H_2S = NH_3.H_2CS_3$$

Action of nascent hydrogen on sulphocyanic acid to furnish methylamine. Decomposition of concentrated sulphocyanic acid, especially on addition of hydrochloric acid, into hydrocyanic and persulphocyanic acids:

$$3HCNS = HCN + H_2C_2N_2S_3$$

Persulphocyanic acid, $H_2C_2N_2S_3$; made by action of gaseous or dissolved hydrochloric acid on saturated solution of ammonium or potassium sulphocyanate. Production of thick jelly, changing into white crystalline magma. Acid almost insoluble in cold, moderately soluble in hot water, and crystallising therefrom in fine yellow needles. Decomposition of its solution by alkalis into sulphocyanate and sulphur.

Persulphocyanogen, $HC_3N_3S_3$; an orange-yellow precipitate produced by action of chlorine or nitric acid on alkali-sulphocyanates. Its conversion by heat into mellon. Its insolubility in ordinary solvents, but dissolution unchanged in oil of vitriol and precipitation therefrom on dilution. Its solubility in alkalis with re-formation of sulphocyanates. Its solution also in sulphydrate of potassium, with evolution of sulphuretted hydrogen and formation of various bodies. Mixed precipitate of sulphur and sulphomelanurate of potassium thrown down on acidifying resulting liquid with acetic acid.

Platinic potassium sulphocyanate $K_2\overset{''''}{Pt}(CNS)_6$, best made by addition of potassium sulphocyanate to hot solution of potassium platinic chloride. Deposition on cooling of dark red crystalline tables:

$$K_2\overset{''''}{Pt}Cl_6 + 6KCNS = K_2\overset{''''}{Pt}(CNS)_6 + 6KCl$$

Platinous potassium sulphocyanate $K_2\overset{''}{Pt}(CNS)_4$, similarly produced from platinous chloride in orange red microscopic needles.

HYDROCYANIC AND CYANIC ETHERS.

Existence of two distinct classes of isomeric hydrocyanic ethers, decomposible, with absorption of water, to yield two distinct sets of products. Existence for example of two ethyl-cyanides, the one decomposible into ethyl-formic (i.e. propionic) acid and ammonia, the other decomposible into formic acid and ethylamine:

$$\begin{array}{rcccrcr} HCN & + & 2H_2O & = & H_2CO_2 & + & H_3N \\ \alpha\text{-}(H_5C_2)CN & + & 2H_2O & = & H(H_5C_2)CO_2 & + & H_3N \\ \beta\text{-}(H_5C_2)CN & + & 2H_2O & = & H_2CO_2 & + & H_2(H_5C_2)N \end{array}$$

Similar existence of two classes of cyanic and sulphocyanic ethers, corresponding to the above two classes of cyanides. Decompositions of the two cyanates of ethyl for instance:

$$\begin{array}{rcccrcr} HCNO & + & 2H_2O & = & H_2CO_3 & + & H_3N \\ \alpha\text{-}(H_5C_2)CNO & + & 2H_2O & = & H(H_5C_2)CO_3 & + & H_3N \\ \beta\text{-}(H_5C_2)CNO & + & 2H_2O & = & H_2CO_3 & + & H_2(H_5C_2)N \end{array}$$

Adhesion of constituent carbon of cyanogen in α-compounds, and of constituent nitrogen in β-compounds, to the ethyl or other alcohol radical. Identity of α-hydrocyanic ethers with the nitriles produced by dehydration of ammonia salts,—of α-cyanide of methyl with acetonitril, and of α-cyanide of ethyl with propionitril, for instance.

α-Methyl cyanide, H_3C_2N or $H_3C.CN$, a thin oily liquid made by heating together cyanide and methyl-sulphate of potassium:

$$K(H_3C)SO_4 \quad + \quad KCN \quad = \quad K_2SO_4 \quad + \quad H_3C.CN$$

Or by heating acetate of ammonia with phosphoric anhydride:

$$H_4C_2O_2.H_3N \quad - \quad 2H_2O \quad = \quad H_3C.CN$$

Fixation of hydrogen upon α-cyanide to produce next higher base, namely ethylamine:

$$H_4 \quad + \quad H_3C.CN \quad = \quad H_2(H_5C_2)N \quad \text{or} \quad H_7C_2N$$

Its combination with hydrochloric or hydriodic acid, after the fashion of ammonia, to form compound $H_3C_2N.HCl$ analogous to $H_3N.HCl$. Its decomposition, with absorption of water, under the influence of caustic alkalis, to produce acetic (methyl-formic) acid and ammonia:

$$H_3C.CN \quad + \quad 2H_2O \quad = \quad H(H_3C)CO_2 \quad + \quad H_3N$$

The α-cyanides of ethyl, amyl, phenyl, &c., strictly analogous bodies, made by analogous processes. Decomposition of α-cyanide of ethyl, for instance, into propionic (ethyl-formic) acid and ammonia.

β-Cyanide of methyl unknown. β-Cyanide of ethyl made by reaction of cyanide of silver and iodide of ethyl in sealed tubes:

$$IH_5C_2 \quad + \quad AgCN \quad = \quad AgI \quad + \quad H_5C_2.CN$$

Also by action of chloroform on ethylamine, in presence of potash:

$$HCl_3C \quad + \quad H_2(H_5C_2)N \quad = \quad 3HCl \quad + \quad H_5C_2.CN$$

Resistance of this cyanide to action of alkalis. Its immediate

decomposition, with absorption of water, under the influence of acids, into formic acid and ethylamine:

$$H_5C_2.CN \quad + \quad 2H_2O \quad = \quad H_2CO_2 \quad + \quad H_2(H_5C_2)N$$

β-Cyanides of amyl and phenyl analogous to that of ethyl.

α-Methyl cyanate unknown. α-Ethyl cyanate made by action of chloride of cyanogen on ethylate of potassium:

$$Na(H_5C_2)O \quad + \quad ClCN \quad = \quad NaCl \quad + \quad H_5C_2.CNO$$

Its decomposition, with absorption of water, under the influence of alkalis, to yield ammonia and ethyl-carbonic acid or its products of decomposition, namely, carbonic acid and alcohol:

$$H_5C_2.CNO \quad + \quad 2H_2O \quad = \quad H(H_5C_2)CO_3 \quad + \quad H_3N$$

Its decomposition by hydrochloric acid into ethyl chloride and cyanuric instead of cyanic acid.

β-Methyl cyanate, a very volatile liquid, made by heating together cyanate and methyl-sulphate of potassium:

$$K(H_3C)SO_4 \quad + \quad KCNO \quad = \quad K_2SO_4 \quad + \quad H_3C.CNO$$

Its decomposition, with absorption of water, under the influence of caustic alkalis, to yield carbonic acid and methylamine:

$$H_3C.CNO \quad + \quad 2H_2O \quad = \quad H_2CO_3 \quad + \quad H_3C.H_2N$$

Its reaction with ammonia to yield methyl-urea, similar to that of cyanic acid yielding normal urea:

$$H_3C.CNO \quad + \quad H_3N \quad = \quad H_3(H_3C)N_2CO$$

Its similar reaction on methylamine to produce dimethyl-urea. Its sudden decomposition by water, probably at two stages, with formation also of dimethyl-urea:

$$\begin{array}{lllllll} H_3C.CNO & + & 2H_2O & = & H_2CO_3 & + & H_2(H_3C)N \\ H_3C.CNO & + & H_2(H_3C)N & = & H_2(H_3C)_2N_2CO & & \end{array}$$

Existence of similar β-cyanates of ethyl, amyl, allyl, phenyl, &c. The cyanurate of ethyl $(H_5C_2)_3C_3N_3O_3$, made by distilling together cyanurate and ethyl-sulphate of potassium, a crystalline compound, decomposible under the influence of caustic potash like the β-cyanate, to yield, however, three molecules of carbonic acid and three molecules of ethylamine. Existence also of diethyl cyanuric acid $H(H_5C_2)_2C_3N_3O_3$.

α-Methyl sulphocyanate $H_3C.CNS$, made by distilling together sulphocyanate and methyl-sulphate of potassium. An alliaceous smelling oil, decomposible under the influence of caustic potash into sulphocarbonic acid or its products of decomposition, and ammonia. Its non-combination with ammonia. The α-ethyl sulphocyanate a similarly produced and reacting compound.

β-Methyl sulphocyanate unknown. β-Ethyl sulphocyanate $H_5C_2.CNS$, made by acting with phosphoric anhydride upon diethyl-sulpho-urea, itself obtained by heating the product of the action of disulphide of carbon upon alcoholic solution of ethylamine. An extremely pungent oily liquid. Its direct combination with ammonia to produce ethyl-sulpho-urea $H_3(H_5C_2)N_2CS$.

Existence of β-sulphocyanate of allyl $(H_5C_3)CNS$, as the essential oil of mustard. Its artificial production by action of allyl iodide upon potassium sulphocyanate. A highly pungent, oily liquid, combining directly with ammonia to produce allyl-sulpho-urea or thiosinamine $H_3(H_5C_3)N_2CS$.

Substitutions of cyanogen for hydrogen or chlorine in various compounds; in urea, for instance, by action upon it of iodide of cyanogen; in acetic acid, by reaction of chloracetic acid and cyanide of potassium; in ethene, by reaction of chloride of ethylen and cyanide of potassium, &c. &c. Frequent exchange, in constituent cyanogen, of N for HO_2 (by its combination with H_3), to furnish higher carbon acids, as in decomposition of α-methyl cyanide. Conversion of cyanacetic into malonic acid; and of cyanide of ethylen into succinic acid; for instance:

$$H_3(CN)C_2O_2 \quad + \quad H_4O_2 \quad = \quad H_4C_3O_4 \quad + \quad H_3N$$
$$H_4(CN)_2C_2 \quad + \quad 2H_4O_2 \quad = \quad H_6C_4O_4 \quad + \quad 2H_3N$$

CYANOGEN AMIDES.

Cyanamide, H_2CN_2 or $H_2N.CN$. Gaseous chloride of cyanogen passed into ethereal solution of ammonia, resulting precipitate of sal-ammoniac filtered off, and cyanamide left in white crystals on evaporation of ethereal solution:

$$ClCN + H_3N = H_2N.CN + HCl$$

Its fusion at 40°, and long retention of liquid state on cooling. Its sudden congelation at 150°, into cyanuramide. Its combination with acids after the fashion of ammonia, to form salts of cyanamide. But deposition of nitrate of urea upon adding nitric acid to its ethereal solution:

$$H_2N.CN + H_2O = H_4N_2CO$$

Cyanuramide, $H_6C_3N_6$ or $(H_2N)_3C_3N_3$, better known as melamine, produced by polymerising of cyanamide; usually made by boiling melam (*vide infra*) with dilute potash until dissolved, evaporating liquid to crystallising point, and letting it cool slowly. Product recrystallised from hot water. Occurrence of cyanuramide in fine white rhombic octahedrons, insoluble in ether and alcohol, sparingly soluble in cold, more so in hot water and still more so in hot solution of potash. Its combination with acids to form crystallisable salts, as the nitrate $H_6C_3N_6.HNO_3$, all having acid reaction to test paper. Its combination with silver nitrate to form similar compound $H_6C_3N_6.AgNO_3$. But its precipitation of most metallic salts after the fashion of ammonia. Its decomposition, when boiled with strong acids, into cyanuric acid and ammonia; and, when heated with fused potash, into cyanic acid and ammonia:

$$3H_2O + (H_2N)_3C_3N_3 = 3H_3N + (HO)_3C_3N_3 \text{ or } 3(HO)CN$$

Existence of amid-hydrates intermediate between melamine and cyanuric acid, namely, ammeline and melanuric acid:

Melamine	$H_6N_6C_3$	or	$(H_2N)_3C_3N_3$
Ammeline	$H_5N_5C_3O$	„	$(H_2N)_2HO.C_3N_3$
Melanuric acid	$H_4N_4C_3O_2$	„	$H_2N(HO)_2C_3N_3$
Cyanuric acid	$H_3N_3C_3O_3$	„	$(HO)_3C_3N_3$

Successive conversion, by treatment with stronger and stronger acids, of melamine into ammeline, of this into melanuric acid, and of this into cyanuric acid, by exchange of peroxide of hydrogen for amidogen or of water for ammonia.

Existence of allied bodies, chlorocyanuramide $(H_2N)_2ClC_3N_3$, a product of the action of cyanuric chloride on ammonia; of sulphomelanuric acid $H_2N(HS)_2C_3N_3$, obtained by a complex process from persulphocyanogen; of ammelide $H_9N_9C_6O_3$, a combination of melanuric acid with ammeline; and of melam $H_9N_{11}C_6$ (or $H_{11}N_{11}C_6O - H_2O$), a combination of ammeline with melamine minus water. Melam the pulverulent greyish white residue left on distilling sulphocyanate of ammonia, or mixed muriate of ammonia and sulphocyanate of potassium. A non-crystallisable compound, yielding melamine and ammeline when boiled with dilute potash, the former crystallising out from the concentrated solution, the latter deposited on acidifying the mother-liquor with acetic acid.

Mellon, $H_3C_6N_9$. Production, by action of greater or less heat on anomalous cyanate of ammonia or urea, on sulphocyanate of ammonia, persulphocyanic acid, sulphocyanogen, melam and the other cyanuramides, of a pale yellow pulverulent residue known as mellon. Compound obtainable most readily from persulphocyanogen, but in greatest purity from melam, ammeline, or cyanuramide:

$$2(H_2N)_2HO.C_3N_3 \quad = \quad (HN)''_3C_6N_6 \quad + \quad H_3N \quad + \quad 2H_2O$$

Mellon insoluble in all ordinary menstrua, including dilute acids and alkalis. Its undecomposibility by any heat short of redness. Its conversion when boiled with concentrated potash into cyameluric acid:

$$(HN)''_3C_6N_6 \quad + \quad 3H_2O \quad = \quad \left.\begin{matrix}(HO)_3\\ N\end{matrix}\right\}C_6N_6 \quad + \quad 2H_3N$$

and when boiled with nitric acid into cyanilic acid:

$$(HN)''_3C_6N_6 \quad + \quad 6H_2O \quad = \quad (HO)_6C_6N_6 \quad + \quad 3H_3N$$

Production of mellonide of potassium $K_3C_9N_{13}$, by ignition of mellon or melam with the sulphocyanate.

Hydromellonic acid, $H_3C_9N_{13}$; made, in solution, by treating with sulphuretted hydrogen mellonide of mercury dissolved in prussic acid. Resulting hydromellonic acid decomposed more or less by evaporation. Its acid reaction, and effervescence with potassium carbonate to produce mellonides. Similar decompositions of mellon into cyameluric acid and di-ammonia, and of hydromellonic acid into cyameluric acid and melamine:

$$(HN'')_3.C_6N_6 \quad + \quad 3H_2O \quad = \quad \left.\begin{matrix}(HO)_3\\ N\end{matrix}\right\}C_6N_6 \quad + \quad (H_3N)_2$$

$$\left.\begin{matrix}(HN'')_3.C_6N_6\\ N'''.C_3N_3\end{matrix}\right\} \quad + \quad 3H_2O \quad = \quad \left.\begin{matrix}(HO)_3\\ N\end{matrix}\right\}C_6N_6 \quad + \quad (H_3N)_2N.C_3N_3$$

Mellonide of potassium $K_3C_9N_{13}$, produced under various circumstances; usually made by adding mellon or melam to fused sulphocyanate of potassium, keeping product for some time at dull red heat and letting it cool slowly. Resulting mellonide crystallised from hot water, and finally from dilute spirit. Its crystallisation with five atoms of water, and resemblance both in taste and appearance to sulphate of quinine. Its solubility in hot, sparing solubility in cold water, and insolubility in alcohol. Its precipitation from heavy metal salts, of respective mellonides. Its decomposition by acetic and hydrochloric acids, with formation of di- and mono-potassium mellonides respectively, $K_2HC_9N_{13}$ and $KH_2C_9N_{13}$. Its decomposition, when boiled with strong potash, into potassium cyamelurate and melamine or an intermediate cyanuric amide.

Cyameluric acid, $H_3C_6N_7O_3$. The potassium salt made by boiling mellon or mellonide of potassium for some time in caustic potash. Conversion of liquid on cooling into crystalline magma. Salt purified by recrystallisation from water. Decomposition of its solution by nitric or hydrochloric acid, with precipitation of cyameluric acid. Acid insoluble in cold, but crystallisable from boiling water. Its formation of acid and neutral salts. Its conversion into cyanilic acid $(HO)_6C_6N_6$, when boiled with nitric acid.

CHAPTER VI.

(56.) Sodium Elements.

Lithium—Sodium—Silver.

Potassium, Rubidium, Cæsium.

Malleable conductive metals, characterised by property of replacing the hydrogen of hydrochloric acid in proportion of atom to atom, to form neutral fusible chlorides, having general formula M′Cl, and atomic heat $6{\cdot}2+6{\cdot}2=12{\cdot}4$. Symbols and atomic weights:

Li	Lithium	7	K	Potassium	39	
Na	Sodium	23	Rb	Rubidium	85	85·7
Ag	Silver	108	Cs	Cæsium	133	

Potassium, rubidium, and cæsium, the most highly basylous of elements, and correlatives of the halogens chlorine, bromine, and iodine. Gradual increase of atomic weight, specific gravity, and basylity, in successive members of the sub-group. Other differences between them similarly gradational.

Lithium, sodium, and silver, much less basylous than the potassium metals; distinguished from them and from one another by various differences.

Triad metals thallium and gold, on account of their each forming a series of monad compounds corresponding to those of potassium and silver, conveniently considered along with the monad metals proper:

Au	Gold	197	Tl	Thallium	204

(57.) Lithium.

Lithium a widely distributed, though far from abundant element. Its chief sources lepidolite or lithia mica, $Al_2O_3.3SiO_2.LiF$, and a mineral spring at Wheal Clifford in Cornwall, containing the chloride. Its existence also as an important constituent of the alumino-silicates, spodumene and petalite; of the aluminous phosphate, amblygonite; of the manganous phosphate, triphylline; and, in smaller quantities, in various micas, felspars, tourmalines, &c. Traces of lithium found in sea-water and most spring waters; in ashes of marine plants, of tobacco, tea, coffee, wood, &c., and of milk, blood and muscular tissue.

Lithium not procurable by ignition of its carbonate with charcoal; but readily by electrolysis of the fused chloride. A lustrous silver-white metal, harder than potassium and sodium but softer than lead; weldable at ordinary temperatures, fusible at 180°. Its sp. gr. 0·578, lower than that of any known liquid. Oxidation of lithium on exposure to air less rapid than that of potassium and sodium. Its preservation in rock oil. Its combustibility in air with brilliant white flame, when heated considerably above its melting point. Its decomposition of water, to yield lithium hydrate, without either fusion of the metal, or inflammation of evolved hydrogen. Brilliant combustion of lithium when thrown upon strong nitric acid. Rapid action of metallic lithium on glass and porcelain at temperatures even below 200°.

Chloride, $LiCl$; made by dissolving lithium hydrate or carbonate in hydrochloric acid, or by decomposing the sulphate with chloride of barium. Unlike chlorides of sodium and potassium an extremely deliquescent salt, soluble in absolute alcohol whether or not mixed with ether, and partially decomposible by ignition in presence of moisture, with formation of lithium hydrate.

Hydrate, $LiHO$; obtained by igniting lithium nitrate in an iron

pot, and dissolving the so produced oxide in water; or by decomposing lithium sulphate with caustic baryta:

$$Li_2SO_4 + Ba(HO)_2 = BaSO_4 + 2LiHO$$

Finely powdered lepidolite ignited with quicklime and chloride of calcium. Resulting chlorides converted into sulphates by treatment with sulphuric acid; and soluble lithium sulphate, having been freed from any calcium sulphate by oxalate of ammonia, decomposed as above. Lithium hydrate a readily fusible, non-volatilisable solid, soluble in water, though far less so than potash or soda, to form a caustic alkaline liquid, yielding well-defined prismatic crystals on evaporation.

Carbonate, Li_2CO_3; a sparingly soluble salt, producible from the hydrate by action of carbonic acid gas; or from the chloride by precipitation with carbonate of potassium or ammonium. Its fusion at a red heat; and partial decomposition at strong red heat, with evolution of carbonic gas.

Sulphate, Li_2SO_4; a soluble, readily crystallisable, neutral salt, made by acting on the crude chloride with sulphuric acid and igniting the product. Existence of a well defined crystalline potassio-sulphate $KLiSO_4$, but not of any hydrogen sulphate.

Phosphate, Li_3PO_4; obtained by precipitation of the sulphate or chloride with caustic soda and phosphate of sodium. Salt very soluble in weak acids, very sparingly soluble in pure water, and practically insoluble in alkaline liquids.

Lithium, in combination, separable from potassium by precipitation of the latter as platino-chloride; separable from sodium and potassium, by dissolution of lithium chloride in mixed alcohol and ether, or by precipitation of lithium phosphate. Characteristic crimson coloration of flame by lithium salts. Spectrum of lithium flame distinguished more particularly by a bright crimson band between lines *B* and *C* of solar spectrum. Existence also of a faint line in the orange, and, at very high temperatures, of a bright line in the blue. Remarkable corrosion of platinum by fused lithium hydrate or carbonate, or by other lithium salt in admixture with carbonate of sodium, attributed to presence of rubidium and cæsium.

(58.) Sodium.

Sodium chloride, by far the most abundant compound of the metal. Its existence, as rock salt, in immense inland deposits; and in sea-water to extent of four ounces in the gallon. Sodium also met with as albite or soda-felspar $Na_2Al_2O_4.Si_6O_{12}$; cryolite $Na_3\overset{'''}{Al}F_6$; tincal $Na_2B_4O_7.10Aq$; trona $Na_4H_2(CO_3)_3.3Aq$; and cubic nitre, $NaNO_3$, &c. More abundant existence of sodium than of potassium compounds in marine plants.

Primary sodium salts—the chloride; also the native borate, carbonate, and nitrate; and, to small extent, the carbonate extracted from ash of sea-weed, &c.

History of production of sodium, same as that of potassium. Metal now made commercially on large scale by strong ignition, in iron cylinders, of intimate mixture of sodium carbonate and charcoal, with some chalk to prevent fusion of mass:

$$Na_2CO_3 \quad + \quad C_2 \quad = \quad Na_2 \quad + \quad 3CO$$

Sodium distilled over, uncombined with carbonous oxide, and solidified in peculiar condenser, formed of two iron plates. Metal purified by fusion under layer of rock oil, and run into moulds. Its preservation under rock oil.

A lustrous metal, of white, with tinge of pink, colour; brittle at 0°, soft and weldable at ordinary temperatures, becoming pasty at 50°, fusing completely at 90°, and boiling below red heat. Crystallisation of sodium after fusion, in quadratic octahedrons.(?) Its sp. gr. of 0·97, slightly above that of potassium. Its oxidisability, on exposure to air, inferior to that of potassium. Consequent practicability of its employment in metallurgy. Ready combustibility of sodium in air or oxygen, chlorine, &c., with characteristic yellow flame. Its withdrawal of chlorous elements from their metallic and other combinations, and consequent use in the manufacture of aluminium, magnesium, silicon, &c.:

$$2NaAlCl_4 \quad + \quad Na_6 \quad = \quad 8NaCl \quad + \quad Al_2$$

Its immediate decomposition of water, alcohols, acids, &c., usually without inflaming:

$$2H_2O \; + \; Na_2 \; = \; 2NaHO \; + \; H_2$$

Its want of action on strong caustic soda solution. Its reaction with fused caustic soda to form the oxide:

$$2NaHO \; + \; Na_2 \; = \; 2Na_2O \; + \; H_2$$

Its formation of a crystalline amalgam with mercury, a liquid alloy with potassium, and solid alloys with various metals.

SODIUM AND HALOGENS.

Chloride, NaCl. Occurrence of deposits of rock-salt in formations of various geologic age, from drying up of inland seas. (?) Those at Wieliczka in Poland, Cordova in Spain, and Cheshire in England the most extensive. Existence also of sodium chloride—disseminated through the soil, as in *steppes* of southern Russia; in various brine springs; and in salt lakes, either rich in other saline matter as the Dead sea, or nearly free from other saline matter as the Utah lake. Presence of about 2·75 per cent. of chloride of sodium in sea-water.

Salt obtained from mines by quarrying, or evaporating down natural or artificial solution; obtained from sea-water by its spontaneous evaporation in shallow ponds (bay salt). Obtained from brine springs by their artificial evaporation, after concentration, by being pumped over stacks of brushwood (*graduation*). Salt produced, or met with, in fine-grained blocks for the table; in coarse crystals for manufacturing purposes; in larger crystals as bay-salt; in massive state, discoloured by clay, as rock salt, and in native crystals, as sal-gem.

Chloride of sodium a white, anhydrous, scarcely deliquescent salt, of sp. gr. 2·08, fusing at a red and subliming at a stronger heat, dissolving in about 3 parts of cold water, and having its solubility scarcely affected by increase of temperature. Boiling point of saturated solution 109·7°. Its crystallisation, by evaporation

of solution, in cubical crystals decrepitating by heat. Its deposition in hydrated hexagonal plates, on cooling solution to -10°. Its immediate precipitation by hydrochloric acid, and ready crystallisation in cubes on cooling hot hydrochloric acid solution. Its crystallisation in octahedrons from aqueous solutions containing urea. Its solubility in rectified spirit but almost insolubility in absolute alcohol.

Decomposition of chloride of sodium, with evolution of hydrochloric acid, by sulphuric, phosphoric, oxalic acids, &c. Decomposition of its vapour by ignited silica, in presence of oxides of hydrogen, aluminium, iron, &c.

$$2NaCl + H_2O + SiO_2 = 2HCl + Na_2O.SiO_2 \text{ or } Na_2SiO_3$$

SODIUM AND OXYGEN, ETC.

Hydrate, $NaHO$; made for special purposes by action of sodium on water; for manufacturing and general purposes by decomposing solution of sodium carbonate with milk of lime, and evaporating down the clear aqueous liquid in iron or silver dishes. Resulting oily liquid at nearly red heat, solidified on cold slabs of metal. Process exactly similar to that for producing hydrate of potassium:

$$Na_2CO_3 + Ca(HO)_2 = CaCO_3 + 2NaHO$$

Hydrate of sodium also made on large scale in alkali-works, by same process of manufacture as the carbonate (*q. v.*). Occurrence of sodium hydrate as a fusible and volatilisable white solid, dissolving freely in water and alcohol to form corrosive strongly alkaline liquids. Separation from strong soda-ley, cooled to 0°, of hydrated crystals $2NaHO.7Aq$. Moderate stability of sodium hydrate under exposure to air, through its conversion externally into non-deliquescent carbonate. Its various reactions, in dissolved state and in dry way, similar to those of potassium hydrate (*q. v.*). Important use of sodium hydrate in manufacture of hard soap. Analysis of organic nitrogenous compounds by their ignition with mixed hydrates of sodium and calcium

(soda-lime). Consequent oxidation of constituent carbon, and correlative hydrogenation of nitrogen into ammonia.

Oxide, Na_2O; producible by exposing the metal to dry decarbonated air; by strongly heating the dioxide; and by heating the hydrate with metallic sodium. A white fusible mass, absorbing moisture to form the hydrate.

Dioxide, Na_2O_2; made by igniting sodium in current of oxygen gas. Friable mass, white when cold, yellow when hot. Its violent reaction with small quantity of water. Its dissolution unchanged when added little by little to excess of cold water. Decomposition of resulting solution by ebullition, into the hydrate and oxygen:

$$Na_2O_2 + H_2O = 2NaHO + O$$

Production of hydrated crystals $Na_2O_2.8Aq$, efflorescing into lower hydrate $Na_2O_2.2Aq$, by continued exposure of solution over oil of vitriol. Decomposition of dissolved dioxide by acids, with evolution of hydrogen peroxide. Its absorption of carbonous oxide to form sodium carbonate, and of nitric oxide to form sodium nitrite:

$$Na_2O_2 + CO = Na_2CO_3$$
$$Na_2O_2 + 2NO = 2NaNO_2$$

Mixture of oxide and dioxide produced by combustion of sodium in air. No tetroxide known.

General similarity of sodium sulphydrate, sulphide, persulphides, amide, and nitride to corresponding compounds of potassium (*q. v.*).

SODIUM OXISALTS.

Nitrate, $NaNO_3$; found native in Peru and Bolivia, as a deposit underlying superficial soil. Salt purified by solution in water, and crystallisation therefrom in obtuse rhombohedrons. Its solubility in little more than its own weight of cold, and still greater solubility in hot water. Boiling point of saturated solu-

tion, 122°. Behaviour of sodium nitrate when heated, either alone or with combustible matter, similar to that of potassium nitrate (*q. v.*). Its use in production of potassium nitrate, as the chief source of nitric acid, and as a manure.

Carbonate, Na_2CO_3; formerly extracted from ash of marine plants known as kelp, barilla, or varec; now produced almost exclusively, and on enormous scale, from common salt, through intervention of sodium sulphate. Common salt, in quantities of half a ton, heated with sulphuric acid in iron pan; and residue of chloride and acid-sulphate of sodium raked on to floor of reverberatory furnace forming part of same construction, known as salt-cake furnace. Action in pan:

$$H_2SO_4 \ + \ 2NaCl \ = \ HNaSO_4 \ + \ NaCl \ + \ HCl$$

Decomposition completed by reverberatory heat; and hydrochloric acid from both stages of operation condensed in coke towers:

$$HNaSO_4 \ + \ NaCl \ = \ Na_2SO_4 \ + \ HCl$$

Residue of sodium sulphate, or salt-cake, then mixed with chalk and pounded coal, and gradually heated to fusion in second reverberatory furnace, known as balling furnace:

$$Na_2SO_4 \ + \ CaCO_3 \ + \ C_4 \ = \ Na_2CO_3 \ + \ CaS \ + \ 4CO\ ?$$

Fused mass of ball soda, or black-ash, cooled in square moulds, broken up, and subjected to systematic lixiviation with water, at temperature not exceeding 45° to avoid decomposition of insoluble sulphide of calcium. Clear but dark solution of carbonate, with much hydrate of sodium (from employment of excess of chalk converted into lime by heat of furnace), evaporated down, and residue roasted in reverberatory furnace, after admixture with sawdust to promote carbonation of the caustic soda. Product known in commerce as soda-ash.

Or carbonate and other salts crystallised away from caustic soda by evaporation of above solution to sp. gr. of 1·5 or so. Current of air then passed through red coloured mother liquor heated under pressure. Its oxidation completed by addition of

nitrate of sodium and evaporation. Heat carried nearly to redness, and resulting fused soda solidified in sheet-iron casks or trays. Crystallisation of sodium carbonate with 10 atoms of water, in large, oblique prismatic, rhomboidal tables, soluble in twice their weight of cold water, and liquefiable in their water of crystallisation. Nauseous taste and alkaline reaction of solution. Salt obtained with 5 atoms of water by its efflorescence in air, or by its crystallisation at temperature of 34°; obtained with 1 atom of water by its crystallisation at 70°—80°, or by boiling down of saturated solution; obtained anhydrous by gentle ignition. Fusion of salt at full red heat; and its scarcely perceptible loss of carbonic gas at intense heat. Its complete decomposition by strong ignition in current of steam:

$$Na_2CO_3 \quad + \quad H_2O \quad = \quad 2NaHO \quad + \quad CO_2$$

Its decomposition by ignition with charcoal, to yield metallic sodium. Soda-crystals more pure than soda-ash, used chiefly for cleansing purposes. Soda-ash used chiefly for conversion into caustic soda by soap-makers; and in manufacture of glass, by fusion of the ash with chalk and sand:

$$Na_2O.CO_2 \quad + \quad CaO.CO_2 \quad + \quad 4SiO_2 \quad = \quad Na_2CaO_2(SiO_2)_4 \quad + \quad 2CO_2$$

Acid-carbonate, $NaHCO_3$; made by passing carbonic acid gas through cold saturated solution of the carbonate; or commercially, by exposing crushed and moistened soda-crystals to atmosphere of carbonic gas. Absorption of the gas with considerable development of heat, so as to expel both adventitious and crystallisation water:

$$Na_2CO_3 \quad + \quad H_2O \quad + \quad CO_2 \quad = \quad 2NaHCO_3$$

Acid-carbonate soluble in not less than ten parts of cold water; whence its capability of being purified by washing away from it of sulphates, chlorides, &c. Its crystallisation in rectangular prisms. Very feebly alkaline reaction of its solution. Salt changed into sesquicarbonate by heating of solution to 100°, and

into simple carbonate by its brisk ebullition. Pure carbonate furnished by ignition of well washed acid carbonate.

Sesquicarbonate $Na_4H_2(CO_3)_3$, precipitable from its solution by cautious addition of alcohol; found native in impure state as *trona*. Its occurrence, crystallised with three atoms of water, in rhombic prisms, intermediate in solubility between the other two carbonates.

Double carbonate of potassium and sodium $KNaCO_3$. Greater fusibility of the two carbonates, mixed in atomic proportions, than of either carbonate separately. Double salt crystallisable with 6 atoms of water.

Sulphate, Na_2SO_4; produced as a residue of many chemical processes, especially of action of sulphuric acid upon nitrate and chloride of sodium (*vide supra*). A neutral salt, crystallising, with 10 atoms of water, in four-sided prisms with dihedral summits. Its efflorescence and reduction to anhydrous state by exposure to dry air. Anomalous solubility of sodium sulphate in water. Its increase of solubility and continuance in decahydrated state up to 34°. Its conversion at 34° into anhydrous salt and gradual decrease of solubility up to 103°, the boiling point of its solution. Production of anhydrous salt in crystals, by raising solution saturated at 34° to boiling point. Maximum solubility in 100 parts of water, of 117 parts of decahydrated salt (equal 55 parts of anhydrous salt) at 34°; and of 42·6 parts of anhydrous salt at 103°. Production of unstable salt with 7 atoms of water, by allowing boiling saturated solution to cool in closed vessels. Property of sodium sulphate to furnish supersaturated solutions. Great manifestation of cold by solution of decahydrated salt in aqueous muriatic acid. Anhydrous salt fusible without change at full red heat.

Acid-sulphate, $NaHSO_4$; the sole product of the action of sulphuric acid upon nitrate and chloride of sodium at moderate temperatures. Compound also formed by action of sulphuric acid on sulphate of sodium. A crystallisable salt, decomposible by alcohol, or much water, into sulphuric acid and sulphate of sodium. Fusion of salt at moderate heat to yield the anhydro-

sulphate. Decomposition of latter at red heat into sulphate and sulphuric anhydride:

$$2NaHSO_4 \text{ or } Na_2SO_4.H_2SO_4 = Na_2SO_4.SO_3 \text{ or } Na_2S_2O_7 + H_2O$$

Existence of complex sulphates $Na_3H(SO_4)_2$, and $K_3Na(SO_4)_2$, the latter known as plate sulphate.

Phosphates. Compound Na_3PO_4, an unstable salt, decomposible by carbonic acid of the air. Di-sodium phosphate Na_2HPO_4, a well known stable salt, existing in the blood and urine, made by saturating crude phosphoric acid, or acid phosphate of calcium, with carbonate of sodium, and crystallising:

$$H_3PO_4 + Na_2CO_3 = Na_2HPO_4 + H_2O.CO_2$$

Occurrence of salt in rhombic prisms, with 12 atoms of water. Its solution in 4 parts of water at 15°. Its fusion, or solution in its water of crystallisation, at 35°. Existence of a heptahydrated salt. Slightly alkaline reaction of disodium phosphate solution. Its decomposition, when boiled with sal-ammoniac, to furnish sodium ammonio-phosphate or microcosmic salt:

$$Na_2HPO_4 + NH_4Cl = Na(NH_4)HPO_4 + NaCl$$

Production of mono-sodium phosphate, as a strongly acid salt, by addition of phosphoric acid to disodium phosphate solution until rendered no longer precipitable by calcium chloride:

$$Na_2HPO_4 + H_3PO_4 = 2NaH_2PO_4$$

Production, by ignition of di- and mono-sodium phosphates, of sodium pyrophosphate and metaphosphate respectively:

$$2Na_2HPO_4 = Na_4P_2O_7 + H_2O$$
$$NaH_2PO_4 = NaPO_3 + H_2O$$

Other important sodium salts, as the hypochlorite, hyposulphite, borates, and silicates, previously described.

Sodium salts, on account of their solubility, not precipitable by ordinary reagents; recognisable by their non-precipitability, fusibility, and marked yellow coloration of flame. Spectrum of

sodium-flame, a simple yellow band identical in position with line *D* of solar spectrum. Sodium distinguished from potassium by its superior specific gravity, notwithstanding its lower atomic weight; by its inferior basylous activity, shown in various ways; by its preferential formation of di-metallic than of mono-metallic phosphate; by the different habit, inferior stability at high temperatures, and inferior solubility and corrosiveness of its carbonate; by the hydration and solubility of its sulphate; and by the solubility of its acid tartrate and platino-chloride. Sodium sometimes recognised by production of crystals of platino-chloride of sodium, on evaporating filtrate from precipitate of platino-chloride of potassium.

(59.) Potassium.

Its chief occurrence in form of nitrate, as an efflorescence upon the soil in Bengal; in form of chloride, dissolved in sea-water; in form of carnalite $KCl.MgCl_2.6Aq$, deposited above bed of rock-salt at Stassfurth in Prussia; very abundantly in form of felspar $K_2Al_2O_4.Si_6O_{12}$, and less abundantly as potash-mica $K_2Al_6O_{10}.Si_6O_{12}$, in primary and stratified rocks. Existence of potash in soils, and especially in clay, from decomposition of felspar. Its concentration in vegetable and animal tissues.

Primary potash-salts—the rough nitrate or saltpetre; the rough chloride, produced from carnalite, from kelp or sea-weed-ash, and from mother-liquor of sea-water; the crude acid-tartrate, tartar or argol, deposited in wine casks; and the carbonate, extracted from wood ashes (pot-ashes), fermented beet-root liquors, suint of sheep-wool, &c. Proposed direct manufacture of the carbonate and hydrate from felspar.

Davy's original production of metallic potassium by electrolysis of moistened hydrate. Early manufacture of potassium by ignition of hydrate with iron borings, and reception of distilled metal in rock-oil:

$$Fe_3 + 4KHO = Fe_3O_4 + K_4 + H_4$$

Its usual production by the strong heating in iron retorts of the

mixed charcoal and carbonate of potassium, resulting from ignition of cream of tartar :

$$K_2CO_3 + C_2 = K_2 + 3CO$$

Inconvenience resulting from combination of produced metal with carbonous oxide, to form solid bodies $K_2C_2O_2$, and an intermediate compound, both liable to explosion. Vapour of metal solidified as quickly as possible in peculiar condenser constructed of two iron plates. Its purification by fusion and forcible filtration under rock-oil, or preferably by redistillation.

Lustrous bluish-white metal, of sp. gr. 0·865; brittle at and below 0°, soft and weldable at ordinary temperatures, melting into a mercury-like liquid at 62·5°, and volatilising in form of green vapour at a red heat. Its crystallisation in obtuse square octohedrons. Its extreme oxidisability, whence its usual preservation under rock-oil; and its ready combustibility in air or oxygen, with characteristic violet flame. Its affinity for chlorine and the halogens. Its withdrawal of oxygen, chlorine, and the more chlorous elements generally, from their various combinations, as with carbon, boron, aluminium, &c. Its immediate decomposition of water, with inflammation of liberated hydrogen :

$$2H_2O + K_2 = 2KHO + H_2$$

Its similar action upon other hydrogenised compounds, especially acids and alcohols. Its want of action, however, upon hydrocarbons. Its combination with sodium to form liquid alloy, and with mercury to form crystalline amalgam.

POTASSIUM AND HALOGENS.

Fluoride, KF; an unstable, soluble, deliquescent salt, combining with hydrofluoric acid to form more stable hydrofluate KF.HF. Alkalinity of solution of fluoride from decomposition:

$$2KF + H_2O = KF.HF + KHO$$

Chloride, KCl; producible by neutralisation of hydrochloric

acid with carbonate of potassium; extracted from kelp or sea-weed-ash, and mother liquor of sea-water; now obtained most abundantly by washing away chloride of magnesium from carnalite $KCl.MgCl_2.6Aq$, with minimum of water. A slightly deliquescent neutral salt, soluble in water and alcohol, crystallising in cubes, fusing at a dull red, and subliming unchanged at a full red heat.

Iodide, KI; made by neutralising hydriodic acid with carbonate of potassium; by decomposing solution of ferroso-ferric iodide, resulting from direct action of iodine on iron, with carbonate of potassium:

$$Fe_2I_6.FeI_2 \text{ or } Fe_3I_8 + 4K_2CO_3 = 8KI + Fe_3O_4 + 4CO_2$$

Also, and most usually, by igniting evaporated product of action of iodine on aqueous potash:

$$5KI + KIO_3 = 6KI + O_3$$

Bromide, KBr; made by similar processes. Both compounds scarcely deliquescent, neutral salts, soluble in water and alcohol, crystallising in opaque cubes, fusing at a moderate and volatilising at a stronger heat.

POTASSIUM AND OXYGEN, ETC.

Hydrate, KHO; producible by action of metal on water, by mutual precipitation of sulphate of potassium and hydrate of barium solutions, and in other ways. Compound usually made by action of milk of lime on carbonate of potassium dissolved in fully ten times its weight of water, and preferably at boiling heat:

$$K_2CO_3 + Ca(HO)_2 = CaCO_3 + 2KHO$$

After subsidence, clear liquid drawn off from precipitate of chalk, evaporated down in iron or silver dishes, and resulting oily liquid at nearly red heat, solidified on cold slab or cast into cylindrical moulds.

Hard, white, semitransparent mass, of sp. gr. 2·2, melting into

clear oil below a red heat, and volatilising undecomposed at full red heat. Its hygroscopicity, deliquescence in moist air, and solution in half its weight of water, with considerable evolution of heat. Its occurrence also in form of deliquescent hydrated crystals KHO.2Aq, dissolving in water with production of cold.

Presence of about 6 per cent. of potash KHO, in pharmacopœial solution of sp. gr. 1·056. Presence of 50 to 60 per cent. in solution of sp. gr. 1·5 to 1·6. Solution of potash, in proportion to its strength, a caustic corrosive liquid, dissolving the cuticle with production of soapy feeling; decomposing fixed oils and fats with formation of soft soaps; and attacking most vegetable and animal matters. Its action upon lead- and other varieties of glass, especially at high temperatures.

Solubility of potash in alcohol. Gradual decomposition and browning of solution. Purified potash obtained by evaporating down the fresh alcoholic solution.

Action of potash on anhydrides to combine with them:

$$CO_2 \;+\; KHO \;=\; KHCO_3$$

Solution, of sp. gr. 1·5, much used in ultimate organic analysis for absorption of carbonic anhydride:

$$CO_2 \;+\; 2KHO \;=\; K_2CO_3 \;+\; H_2O$$

Analogous action of fused potash on aluminic, silicic, &c., oxides and anhydrides; also on glass and porcelain:

$$SiO_2 \;+\; 2KHO \;=\; K_2SiO_3 \;+\; H_2O$$

Action of potash on acids to neutralise them, with elimination of water. Titration of acids by alkalis:

$$H_2SO_4 \;+\; 2KHO \;=\; K_2SO_4 \;+\; 2H_2O$$

Its action on salts of ammonia and alkaloïds to liberate ammonia or alkaloïd:

$$H_3N.HCl \;+\; KHO \;=\; KCl \;+\; H_3N \;+\; H_2O$$

Its action on most metallic salts to throw down insoluble hydrates or oxides:

$$ZnCl_2 + 2KHO = 2KCl + Zn(HO)_2$$
$$HgCl_2 + 2KHO = 2KCl + HgO + H_2O$$

Resulting aluminium, chromium, zinc, lead, and tin hydrates soluble in excess of aqueous potash. From solutions of certain metallic salts, basic salts, or compounds of normal salt with oxide or hydrate, thrown down by deficit of alkali.

Action of potash as an oxidising agent, with correlative evolution of hydrogen. Its solution of metals zinc and aluminium for instance:

$$\overset{\prime\prime}{Zn} + 2KHO = K_2\overset{\prime\prime}{Zn}O_2 + H_2$$
$$\overset{\prime\prime\prime}{Al}_2 + 6KHO = 2K_3\overset{\prime\prime\prime}{Al}O_3 + 3H_2$$

Its somewhat similar action, when in fused state or in alcoholic solution, upon many oxidisable organic compounds to form potassium salts of produced organic acids. Its action on wood-spirit and benz-aldehyd for instance to produce potassium formiate and benzoate respectively:

$$H_4CO + KHO = KHCO_2 + 2H_2$$
$$H_6C_7O + KHO = KH_5C_7O_2 + H_2$$

Destructive oxidation of woody fibre by heated caustic potash, with production of potassium oxalate:

$$H_{10}C_6O_5 + H_2O + 6KHO = 3K_2C_2O_4 + 9H_2$$

Oxides of potassium unimportant compounds. The protoxide K_2O, made by exposing potassium to air, carefully freed from moisture and carbanhydride. Also by heating the hydrate with potassium:

$$2KHO + K_2 = 2K_2O + H_2$$

A white, fusible, volatile solid, deliquescing in moist air, and becoming incandescent when moistened with water. The tetroxide K_2O_4, a yellow powder or soft mass, made by exposing moderately heated potassium to a current at first of dry air and

then of oxygen. Its deliquescence in moist air, and decomposition by water, with evolution of oxygen and formation of potassium dioxide in solution. The solid dioxide K_2O_2, a white powder, not isolable in pure state, but formed in process for making the tetroxide. Its reaction with hydrochloric acid to yield peroxide of hydrogen:

$$K_2O_4 + 2HCl = H_2O_2 + 2KCl$$

Mixture of tetroxide with lower oxides produced by combustion of potassium in air or oxygen.

Sulphydrate, KHS; made by saturating dissolved potash with sulphuretted hydrogen and evaporating down. A deliquescent colourless salt, occurring in well-defined hydrated prismatic crystals; and in fused masses, undecomposible by ignition out of access of air. Its solubility in water and alcohol to form colourless, alkaline, caustic liquids, decomposible by all acids, including carbonic acid, by oxygen of the air, and by sulphur:

$$H_2CO_3 + KHS = KHCO_3 + H_2S$$
$$2KHS + O \text{ or } S = K_2S_2 + H_2O \text{ or } H_2S$$

Its action on most metallic salts to throw down insoluble sulphides, and evolve sulphuretted hydrogen, sometimes absorbed by excess of metallic salt:

$$FeSO_4 + 2KHS = K_2SO_4 + FeS + H_2S$$

Sulphide, K_2S; said to be produced in solution by half saturating dissolved potash with sulphuretted hydrogen:

$$KHS + KHO = K_2S + H_2O$$

Colourless alkaline liquid, decomposible by acids and becoming yellow by exposure to air like the sulphydrate. Its solution of sulphur, and reaction with metallic salts, unattended by evolution of sulphuretted hydrogen.

Indefinite sulphide, resulting from ignition of sulphate of potassium with charcoal or hydrogen, sometimes pyrophoric.

Di-, tri-, and tetra-sulphides, K_2S_2, K_2S_3, and K_2S_4, yellow fusible compounds, resulting from definite reactions, forming

orange-yellow solutions, and otherwise resembling the pentasulphide. The impure trisulphide, made by igniting mixture of carbonate of potassium and sulphur, known as liver of sulphur.

Pentasulphide, K_2S_5; made by heating hydrate, sulphydrate, and inferior sulphides of potassium with sufficiency of sulphur. Separation of excess of sulphur as a distinct stratum, overlying fused mass of pentasulphide. The latter a liver-brown resinous-looking substance, deliquescing and otherwise altering on exposure to air, and dissolving in water to form a deep orange solution. The pentasulphide in solution, together with hyposulphite of potassium, also formed by boiling excess of sulphur in aqueous potash:

$$S_6 + 3KHO = K_2S_5 + KHSO_2 + H_2O$$

Alkaline reaction of pentasulphide solution. Its absorption of carbanhydride from the air, with evolution of sulphuretted hydrogen. Its immediate decomposition by addition of stronger acid, with evolution of sulphuretted hydrogen and precipitation of sulphur:

$$K_2S_5 + 2HCl = H_2S + S_4 + 2KCl$$

Its decomposition, however, when added to excess of hydrochloric acid, to yield persulphide of hydrogen as a heavy oil, holding excess of sulphur in solution:

$$K_2S_5 + 2HCl = H_2S_3 + S_2 + 2KCl$$

Its reaction with most heavy-metal salts to precipitate either persulphides or mixtures of sulphides and sulphur:

$$K_2S_5 + PbCl_2 = PbS_2 + S_3 + 2KCl$$

Its oxidation, on exposure to air, with formation of hyposulphite and separation of sulphur:

$$K_2S_5 + H_2O + O_3 = 2KHSO_2 + S_3$$

Amide, KH_2N; an olive-green, easily fusible substance, made by gently heating potassium in current of dry ammonia:

$$2H_3N + K_2 = 2KH_2N + H_2$$

Its combustibility in air or oxygen, to furnish potassium hydrate, &c.:

$$2KH_2N + O_3 = 2KHO + H_2O + N_2$$

Its reaction with water, to form potassium hydrate and ammonia:

$$H_2O + KH_2N = KHO + H_3N$$

Intermediate compound, K_2HN, unknown. The nitride K_3N, made by heating the amide to a little below redness out of contact with air:

$$3KH_2N = K_3N + 2H_3N$$

A nearly black, infusible solid, frequently taking fire on exposure to air. Its reaction with water similar to that of the amide:

$$3H_2O + K_3N = 3KHO + H_3N$$

POTASSIUM OXISALTS, ETC.

Nitrate, KNO_3; found disseminated through superficial soil, or effloresced upon its surface, in parts of Bengal. Salt extracted by lixiviating the soil with water, filtering liquid through wood ashes, and boiling down. Nitre also produced by decomposing artificially formed calcium nitrate with wood-ashes (carbonate of potassium); and by decomposing native sodium nitrate with potassium chloride (*vide* p. 73). Potassium nitrate, nitre, or saltpetre, a white, anhydrous, non-deliquescent salt, having a cooling saline taste. Its crystallisation in hexagonal prisms with dihedral summits; but occasionally in heteromorphous form of minute rhombohedrons, isomorphous with those of sodium nitrate. Its solubility in 3·5 times its weight of cold, and 0·3 of its weight of boiling water. Refinement of nitre by its deposition, during cooling of hot concentrated solution under continual agitation, in form of nitre meal, afterwards washed successively with cold saturated solution of nitre, and with cold water. Insolubility of nitre in absolute alcohol. Its fusion unchanged below a red heat, and solidification on cooling into hard transparent masses.

Its decomposition at a red heat into potassium nitrite and oxygen. Its complete decomposition at a full red heat, with evolution of nitrogen and some oxygen, to leave residue of ill-defined peroxide of potassium. Chief use of nitre as the oxidising constituent of gunpowder. Its similar use in the manufacture of slow matches, touch-paper, &c. General employment of nitre in the laboratory as an oxidising or deflagrating agent. Production, for instance, of potassium carbonate, sulphate, arsenate, &c., by deflagrating carbon, sulphur, arsenic, &c., with nitre.

Nitrite, KNO_2; made by heating the nitrate to redness, dissolving product in water, crystallising out unchanged nitrate, and evaporating residuary solution to dryness. An anhydrous, deliquescent, and difficultly crystallisable salt.

Chlorate, $KClO_3$; produced by transmitting excess of chlorine through aqueous caustic potash, or preferably through mixed milk of lime and chloride of potassium, and boiling:

$$6KHO + Cl_6 = 5KCl + KClO_3 + 3H_2O$$
$$KCl + 3CaH_2O_2 + Cl_6 = 3CaCl_2 + KClO_3 + 3H_2O$$

In either case, the sparingly soluble chlorate separated from the very soluble chloride by crystallisation, and purified by recrystallisation. Its solubility in 16 parts of cold, and in less than 2 parts of boiling water. Its deposition, on cooling hot saturated solution, in anhydrous non-deliquescent rhomboïdal tables. Fusion and decomposition of potassium chlorate, at moderate heat into perchlorate, chloride, and oxygen, at stronger heat into the chloride and oxygen:

$$KClO_3 = KCl + O_3$$

The chlorate a more powerful oxidising and deflagrating agent than the nitrate. Production of potassium manganate, ferrate, &c., by heating oxide of manganese or iron with mixed chlorate and hydrate of potassium. Easy explosion by friction, as in a mortar, of mixtures of potassium chlorate with sulphur, phosphorus, sulphide of antimony, &c. Use of the chlorate in manufacture of lucifer matches, friction tubes, percussion caps, &c. De-

composition of the chlorate by sulphuric, nitric and hydrochloric acids, with evolution of chlorine or its oxides. Frequent use of mixed hydrochloric acid and chlorate of potassium as an oxidising agent in the moist way.

Perchlorate, $KClO_4$; made by gently heating the chlorate so as to expel about 10–13 per cent. of its weight as oxygen:

$$2KClO_3 = KClO_4 + KCl + O_2$$

Residue dissolved in boiling water, and perchlorate crystallised out. Salt also formed by action of nitric or sulphuric acid on the chlorate. Perchlorate of potassium anhydrous, non-deliquescent, freely soluble in hot, very sparingly soluble in cold water. Its superiority to the chlorate in stability, and consequent inferiority to it for explosive uses. Its decomposition at a red heat into the chloride and oxygen:

$$KClO_4 = KCl + O_4$$

Carbonate, K_2CO_3. Wood burnt in heaps upon the ground, in pits, or in fire-places. Ashes sifted and lixiviated in barrels, with or without lime. Solution, sometimes after separation of more insoluble salts, evaporated down to dryness, usually in iron pots, and residue (or black ash) ignited for some hours. Resulting fused, and more or less coloured, mass of carbonate known as potash or potashes. By ignition of black ash in reverberatory furnaces, the carbonate obtained in white granules, known as pearlash. Refined pearlash, or salt of tartar, made by extracting the carbonate from pearlash by deficit of cold water, evaporating down solution and calcining residue; or by completely dissolving pearlash in hot water, separating more insoluble salts by crystallisation, and evaporating down and calcining the mother-liquor. Variation in details of production as conducted in different countries.

Molasses of beet-root, after separation of crystallisable sugar, fermented, alcohol distilled off, watery liquor evaporated down, residue concentrated, and resulting crude potash refined.

Various vegetable matters treated in more or less similar manner.

Washings of sheep's wool evaporated down and incinerated, &c. Production of 7 or 8 pounds of soda-free carbonate of potassium from every 100 lb. of raw wool. Some carbonate of potassium made from the sulphate, &c., by Leblanc's soda process; and in other ways. The pure carbonate made by ignition either of the crystalline acid-carbonate, or of cream of tartar, alone or in admixture with nitre.

Carbonate of potassium an anhydrous compound, fusing at a red, and volatilising at an intense heat. Reaction of the fused carbonate with silica, alumina, &c., to form soluble silicates and aluminates by expulsion of carbanhydride, whence its use in analysis of siliceous minerals:

$$K_2CO_3 \quad + \quad Al_2O_3 \quad = \quad K_2Al_2O_4 \quad + \quad CO_2$$

Solubility of carbonate of potassium in rather more than an equal weight of cold, and in less than half its weight of boiling water, to form alkaline caustic liquids, yielding hydrated crystals, $K_2CO_3.2Aq$. Its insolubility in alcohol. Its hygroscopicity, shown by its deliquescence in moist air, and dehydration of spirit of wine. Decomposition of dilute aqueous solution by milk of lime, with formation of caustic potash. Decomposition of fused salt to but slight extent, by its ignition in current of steam. Its decomposition by ignition with charcoal, to yield metallic potassium.

Acid- or hydro-carbonate, $KHCO_3$; deposited in rhombic prisms, on passing current of carbonic acid gas through saturated solution of the carbonate. A very pure salt, permanent in the air, soluble in 4 times its weight of cold water to form a neutral solution, evolving carbonic acid on exposure to air, and rapidly on ebullition. Its conversion into the normal carbonate by ignition.

Sulphate, K_2SO_4; producible by action of sulphuric acid on carbonate, nitrate, chloride, &c. of potassium (*vide infra*). Usually obtained from mother-liquors of sea-water, or from solution of sea-weed ash (kelp or varec). A neutral salt, occurring in hard, non-deliquescent, anhydrous, six-sided, pyramidal crystals, freely soluble in hot, sparingly soluble in cold water,

and insoluble in alcohol. Its fusion unchanged at a full red heat. Its reaction with most stronger acids to form the hydrogen sulphate:

$$K_2SO_4 + HCl = KHSO_4 + KCl$$
$$K_2SO_4 + H_2SO_4 = 2KHSO_4$$

Its combinations with sulphates of the aluminium and magnesian class, to form well-defined double salts, such as:

$$K_2SO_4.MgSO_4.6Aq \quad \text{or} \quad K_2M\overset{''}{g}(SO_4)_2.6Aq$$
$$K_2SO_4.Al_2(SO_4)_3.24Aq \quad \text{or} \quad 2K\overset{'''}{Al}(SO_4)_2.12Aq$$

Acid- or hydro-sulphate, $KHSO_4$; producible as above, by action of stronger acids upon the neutral sulphate; also by action of sulphuric acid on nitrate or chloride of potassium, at a gentle heat:

$$KNO_3 + H_2SO_4 = HNO_3 + KHSO_4$$

Formation, however, of neutral sulphate by reaction, at higher temperature, of first produced acid-sulphate on excess of the nitrate or chloride:

$$KNO_3 + KHSO_4 = HNO_3 + K_2SO_4$$

A very soluble, strongly acid salt; effervescing with carbonate of potassium to form the neutral salt:

$$K_2CO_3 + 2KHSO_4 = H_2O.CO_2 + 2K_2SO_4$$

Crystallisation of the acid-sulphate from its hot solution in rhombic octahedrons, and by way of fusion in rhombic prisms. Its decomposition by alcohol, or by much water, into sulphuric acid and the neutral sulphate:

$$2KHSO_4 = H_2SO_4 + K_2SO_4$$

Its fusion unchanged at a moderate heat, but evolution at higher temperatures, of water, and then of sulphuric acid and

anhydride, so as to leave the neutral salt. Use of acid-sulphate of potassium as a flux in mineral analysis.

Formation of anhydro-salt, $K_2SO_4.SO_3$, or $K_2S_2O_7$, in prismatic needles, by acting on the normal salt with excess of strong sulphuric acid. Its dissolution unchanged in small quantity, but decomposition by a larger quantity of water to form the hydrogen sulphate.

Existence, in addition to above simple hydrogen sulphate, $KHSO_4$ or $K_2H_2(SO_4)_2$, of the unstable double salts, $K_2H(SO_4)NO_3$, and $K_2H_3(SO_4)PO_4$, producible by respective actions of nitric and phosphoric acids on sulphate of potassium.

Phosphates. Compounds K_3PO_4, and K_2HPO_4, ill-defined or unstable alkaline salts, decomposible by carbonic acid. The acid- or di-hydrogen phosphate, a stable well-defined salt, made by nearly neutralising crude phosphoric acid with carbonate of potash and crystallising. Its deposition in dimetric prisms, soluble in water, insoluble in alcohol. Sour taste and acid reaction to litmus paper of the aqueous solution, but re-assumption of blue colour by the reddened paper on becoming dry. Salt unchanged by heat of 200°. Its fusion at a red heat into clear glass of potassium metaphosphate:

$$KH_2PO_4 \quad - \quad H_2O \quad = \quad KPO$$

Potassium salts recognised by their fusibility, and by their violet coloration of flame; showing, when analysed by the prism, a bright line in the red *A*, together with a fainter line in the red and another in the violet, of an almost continuous spectrum. Neutral solutions of potassium salts precipitated by tartaric acid, as cream of tartar, $KH_5C_4O_6$; and by perchloride of platinum and hydrochloric acid, as platinochloride of potassium, K_2PtCl_6. Both precipitates crystalline, insoluble in alcohol, sparingly soluble in cold, and moderately soluble in boiling water.

(60.) Rubidium and Cæsium.

Compounds of the two metals widely, though very sparingly, distributed; in certain minerals, as lepidolite and other forms of mica; in mineral springs, as those of Durkheim and Nauheim; and the former metal in vegetable ashes, as those of beetroot and tobacco. Cæsium usually less abundant than rubidium, but found to extent of 32 per cent. in a rare mineral from Elba, known as Pollux.

Mixed platinochlorides of potassium, rubidium, and cæsium, freed from potassium by prolonged boiling in water. Residue heated in current of hydrogen, and chlorides of rubidium and cæsium extracted by water. Chlorides converted into sulphates by treatment with sulphuric acid; sulphates into hydrates by baryta-water; and hydrates into carbonates by carbonic acid. By suitable addition of tartaric acid to carbonates, rubidium converted into insoluble acid-, and cæsium into deliquescent neutral tartrate.

Rubidium distilled from charred acid-tartrate, as a soft white metal, of sp. gr. 1·52, melting at 101·3, and volatilising in greenish blue vapour below red-heat. Its oxidisability decidedly greater than that of potassium, shown by its taking fire on exposure to air, as well as when brought in contact with water.

Metallic cæsium known only in form of its electrolytically obtained amalgam, more positive than that of rubidium.

Correspondence of hydrates, chlorides, nitrates, and sulphates of rubidium and cæsium to those of potassium. Combinations of sulphates with sulphate of aluminium to form readily crystallisable alums. Carbonates of both metals soluble, deliquescent, strongly alkaline salts, absorbing carbonic acid from the air. That of cæsium soluble in boiling absolute alcohol. Platinochlorides nearly insoluble even in boiling water—that of cæsium most so. Acid-tartrates slightly soluble—that of cæsium most so.

Spectrum of ignited rubidium compounds characterised by presence of two red lines beyond potassium line *A*, and by two

faint violet lines; that of cæsium by two very bright lines in the blue. Same violet coloration of flame by rubidium and cæsium salts as by those of potassium.

(61.) Thallium.

Thallium, though a rare element, distributed far more abundantly than, and almost as widely as, lithium, rubidium and cæsium. Its non-recognition in the vegetable kingdom; its principal occurrence in some varieties of iron and copper pyrites, of zinc blende, and of lepidolite; also in the saline residues of salt-works at Nauheim. Its extraction from all these sources. Its most economical production from the flue-dust of pyrites burners: *i.e.* from the metalliferous dust deposited in long flues intervening in some oil of vitriol factories between the pyrites burners and leaden chambers. Dust exhausted with boiling water, and resulting solution treated with considerable excess of hydrochloric acid, so as to precipitate thallium in form of its almost insoluble chloride. Acid-sulphate then obtained from crude chloride by dissolving it in hot sulphuric acid, and driving off excess of acid by heat. Solution of fused acid residue, after treatment with excess of sulphuretted hydrogen to remove arsenic, lead, and other foreign metals, boiled, supersaturated with ammonia, filtered from any precipitate of iron oxide, &c., and evaporated down. Sulphate of thallium then crystallised out from sulphate of ammonium, and purified by recrystallisation. Metallic thallium obtainable from the sulphate by electrolysis of its solution, or, preferably, by reducing it with plates of zinc. Spongy mass of reduced metal washed with water, squeezed dry, melted in atmosphere of coal-gas, or under flux of potassium cyanide.

Thallium, a highly lustrous, nearly white metal, tarnishing instantly, but only superficially, on exposure to air. Its sp. gr. 11·8–11·9. Its extreme softness even at $-18°$, capability of being scratched even by lead, of giving a streak to paper, and of being welded by pressure. Resemblance of thallium to lead in sp. gr., softness, malleability, and want of ductility, tenacity,

and elasticity. Thallium wire difficultly producible by drawing, readily by pressure (squirting). Crystallisation of thallium, after fusion, in octahedral and fern-like forms; crystalline habit of metal shown by its crackling when burnt, and exhibiting moiré after action of water. Its fusion, without becoming pasty, at 294°, and considerable contraction on solidification. Its partial volatilisation at a red heat, ebullition below a white heat, and ready distillation in a current of hydrogen. Thallium intermediate between tin and lead in conductivity, and highly diamagnetic.

Considerable oxidation of thallium as of lead, when heated in a current of air; resulting oxide, like litharge, readily fusible and absorbable by bone-ash cupel. Brilliant combustion of metal in oxygen. Its rapid oxidation by conjoint action of air and moisture, but permanency in non-oxygenated water, and, save for superficial tarnish, in dry air. Thallium readily attacked by nitric acid, dissolved but slowly by sulphuric acid, and scarcely at all by hydrochloric acid, even when boiling.

Formation by thallium of two distinct sets of compounds, monadic, typified by thallous chloride $TlCl$; and triadic, typified by thallic chloride $TlCl_3$; also of various intermediate compounds.

THALLOUS COMPOUNDS.

Chloride, $TlCl$; produced by action of deficit of chlorine on metallic thallium; usually made by precipitating some dissolved thallous compound with hydrochloric acid or a soluble chloride. White clotty precipitate, moderately soluble in and crystallisable from boiling water. Its fusion at a little over 260°, and volatilisation at higher temperatures. Its partial volatilisation in vapour of water. Solidification of melted chloride into white, crystalline, slightly flexible mass, reducible by zinc and dilute acid, like fused chloride of silver. Darkening of thallous chloride under exposure to sunlight. Its combination with platinum chloride to form yellow crystalline insoluble double salt Tl_2PtCl_6.

Iodide, TlI; formed by treating dissolved thallous salts with iodide of potassium, as a bright yellow, occasionally, when thrown down from hot solutions, crystalline, precipitate, practi-

cally insoluble in water. Its fusion below red-heat into scarlet liquid, congealing into scarlet solid, becoming after some time, or upon friction, yellow.

Hydrate, TlHO; made by allowing the metal to oxidise in moist air, boiling product in water, and evaporating down solution. Some white carbonate deposited first, and then the hydrate in yellow needles. Compound also formed, as a bright yellow mass, by decomposing thallous ethylate (thallium alcohol) with water:

$$TlEtO + H_2O = HEtO + TlHO$$

Thallous hydrate a powerful base, dissolving in water to form a colourless strongly alkaline liquid absorbing carbonic acid from the air, neutralising acids, precipitating metallic salts, and expelling ammonia from ammonia salts, after the manner of potash. Its corrosion and staining of the cuticle. Precipitation of its thallium by hydrochloric acid, iodide of potassium, and sulphide of ammonium.

Oxide, Tl_2O; formed by exposing thallous hydrate in vacuo over oil of vitriol. A reddish-brown mass, melting into a brown limpid liquid, solidifiable into an almost black crystalline solid. Its evolution of vapour when more strongly heated, and partial oxidation into the peroxide. Its dissolution in water to re-form the hydrate.

Sulphide, Tl_2S; thrown down from thallous salts by sulphide of ammonium, as a brown precipitate insoluble in aqueous sulphuretted hydrogen and sulphide of ammonium, but dissolving in water through oxidation; and readily soluble in sulphuric acid with evolution of sulphuretted hydrogen.

Nitrate, $TlNO_3$; a soluble crystalline salt, made by dissolving metallic thallium in nitric acid, and evaporating solution.

Carbonate, Tl_2CO_3; deposited as a crystalline precipitate upon exposing solution of thallous hydrate to the air; made by boiling oxidised thallium with solution of ammonium carbonate and crystallising. White anhydrous prismatic crystals, fusing at a moderate heat, sparingly soluble in cold, more soluble in hot water, to form an alkaline liquid.

Sulphate, Tl_2SO_4; made by decomposing the chloride or nitrate with sulphuric acid. A white, tolerably soluble, easily crystallisable, anhydrous salt, isomorphous with sulphate of potassium. Its combination with sulphate of aluminium to form thallium-alum $TlAl(SO_4)_2.12Aq$, and with sulphate of magnesium to form complex sulphate $Tl_2Mg(SO_4)_2.6Aq$, both isomorphous with corresponding potassium compounds.

Ethylate, $Tl(H_5C_2)O$; made by exposing thallium simultaneously to vapour of absolute alcohol and oxygen gas. When freed from excess of alcohol, an oily liquid, having a sp. gr. 3·5, greater than that of any other known liquid, except mercury. Its solidification at $-3°$, and decomposition at 130° and upwards. Its solubility in anhydrous alcohol and ether, and decomposibility by moisture with formation of thallous hydrate.

THALLIC COMPOUNDS.

Chloride, $TlCl_3$; made by treating the lower chlorides, or thallium itself, with excess of chlorine. Fusion of product at gentle heat, with some loss of chlorine. Its free solubility in water, and production in form of hydrated colourless crystals $TlCl_3.Aq$, by vaporisation of its solution in vacuo. Its combination with chlorides of alkali-metals to form double salts as $3KCl.TlCl_3$; $3NH_4Cl.TlCl_3$, &c. Its similar combination with thallous chloride to form double salts $3TlCl.TlCl_3$ or Tl_4Cl_6, and $TlCl.TlCl_3$ or Tl_2Cl_4, the so-called sesquichloride and dichloride of thallium respectively. The sesquichloride a well defined highly crystalline compound, producible in very sparingly soluble hexagonal scales by oxidising thallous chloride with nitro-muriatic acid, or reducing thallic chloride by cautious addition of sodium sulphite. Its decomposition by platinic chloride into thallous chloride, precipitated as double salt $2TlCl.PtCl_4$, and thallic chloride $TlCl_3$, left in solution. Its decomposition by aqueous ammonia into thallous chloride and thallic hydrate:

$$3TlCl.TlCl_3 + 3NH_4HO = 3TlCl + 3NH_4Cl + TlHO_2 + H_2O$$

Its reduction by gaseous ammonia at a gentle heat:

$$3Tl_4Cl_6 \;+\; 8NH_3 \;=\; 12TlCl \;+\; 6(NH_3.HCl) \;+\; N_2$$

Oxide, Tl_2O_3; *obtained by decomposing thallic salts with* ammonia, potash, or thallous hydrate, and drying original precipitate of thallic hydrate, at 260°:

$$2TlHO_2 \;=\; Tl_2O_3 \;+\; H_2O$$

Some thallic oxide formed by ignition of thallium in air, and especially in oxygen. A dark brown, difficultly fusible powder, insoluble in water and alkalis, but dissolving in acids to form thallic salts. Its reduction by strong ignition into thallous oxide.

Sulphate, $Tl_2(SO_4)_3$; a crystallisable salt, both in anhydrous form and with 7 atoms of water, made by dissolving thallic oxide or hydrate in dilute sulphuric acid. Partial decomposition of salt by water, with precipitation of thallic hydrate. Its combination with sodium sulphate to form crystalline double salt $NaTl'''(SO_4)_2$.

Thallium associated with potassium by the characters of thallous platino-chloride, acid-tartrate, sulphate, and alumino-sulphate. Thallous hydrate distinguished from potassium hydrate by its ready decomposibility into oxide and water. Thallous chloride, iodide, and sulphide distinguished from corresponding potassium compounds by their insolubility or sparing solubility. Metal distinguished from potassium by its high atomic weight, high specific gravity, and permanency in both air and water separately. Also by its ready reducibility from its salts, either by metallic zinc in the moist way, or by their ignition with carbonate of sodium and charcoal.

Relationship, in properties and position, of triad thallium to monad potassium and cæsium, strictly parallel to that of tetrad lead to diad calcium and barium. Poisonous character of thallium salts similar to that of lead salts:

K 39	KCl	Ca 40	$CaCl_2$
Cs 133	CsCl	Ba 137	$BaCl_2$
Tl 203	TlCl and $TlCl_3$	Pb 207	$PbCl_2$ and $PbCl_4$

Thallium compounds characterised by their intense green coloration of flame. Spectrum of thallium flame constituted entirely of one bright green band. Thallous salts recognisable by their precipitability by sulphide of ammonium, iodide of potassium, and hydrochloric acid, and their non-precipitability by alkalis. Thallic salts recognisable by their non-precipitability by hydrochloric acid, and ready precipitability by alkalis. Thallous and thallic salts mutually transformable by actions of chlorine and sulphurous acid respectively.

(62.) Silver.

Found native as crystalline or fibrous silver; also alloyed with gold, mercury, copper, and semi-metals. Its chief ore the sulphide, or silver-glance Ag_2S. Existence of numerous double sulphides, as silver-copper-glance $AgCúS$, myargyrite $AgSbS_2$, the red silvers Ag_3AsS_3 and Ag_3SbS_3, polybasite Ag_9SbS_6, psaturose $Ag_{12}Sb_2S_9$, &c. Presence of some sulphide of silver in ordinary galena or lead sulphide, and in fahlerz or argentiferous copper ore. Mutual replacement, to greater or less extent, of silver sulphide Ag_2S, and cuprous sulphide Cu_2S, in many minerals, including silver-copper-glance, polybasite, &c. Occurrence of silver in forms of iodide, bromide, chlorobromide, and chloride, the last known as horn-silver. Its existence in sea-water.

Silver extracted from argentiferous lead by crystallisation and cupellation, and from argentiferous copper by liquation and cupellation.

Amalgamation processes. At Freyburg, pyrites containing silver-sulphide roasted in reverberatory furnace with 10 per cent. of common salt. Roasted mass ground to fine powder, mixed with water, and agitated with scrap-iron in revolving casks. Reduced silver extracted by mercury. Excess of mercury strained off from fluid amalgam, and remainder distilled off from pasty residue, leaving spongy mass of silver alloyed with copper. In Mexico and Chili, crushed mineral containing sulphide and metallic

silver, ground to powder, moistened, and mixed with common salt by treading of horses. Some rough sulphate of copper or *magistral* afterwards added, and mixture incorporated with mercury by treading. Resulting solid amalgam extracted by more mercury, and fluid amalgam treated as above. Reaction of common salt and magistral, &c., to form sodium sulphate and cuprous chloride. Reaction of cuprous chloride and silver sulphide to form silver chloride and cuprous sulphide. Silver-chloride dissolved by excess of common salt, and reduced by mercury, with formation of calomel. Duration of process many weeks.

Non-mercurial processes. Sulphide ores roasted alone and afterwards with common salt. Resulting chloride of silver dissolved in concentrated solution of salt, and precipitated by metallic copper. Or sulphide ores roasted alone at gradually increasing temperatures so as to effect decomposition of intermediately produced sulphates of copper and iron. Unaltered sulphate of silver then extracted from residuary copper and iron oxides by boiling water, and its solution precipitated by metallic copper.

Fine silver obtained by dissolving the metal in nitric acid, diluting with water, and precipitating filtered solution with common salt. Resulting chloride of silver thoroughly washed by decantation and, after mixture with a little sulphuric acid, reduced by bars of zinc. Deposit of silver finally digested in dilute sulphuric acid, washed, dried, and cast into ingots. Further purification of silver by precipitating redissolved metal with hydrochloric acid, and reducing washed chloride by fusion with alkali-carbonate or mixture of chalk and charcoal.

Silver, a brilliant, white, tenacious, ductile, malleable, highly conductive metal, intermediate between copper and gold in hardness, but becoming much harder by admixture with copper. Its crystallisation in the regular system. Sp. gr. 10·53. Its fusion at a full red heat, and volatilisation at an intense heat, with production of green vapour. Solid and liquid silver unoxidisable in dry or moist air, but its vapour combustible in air

or oxygen. Absorption by pure fused silver of 22 times its volume of oxygen gas, discharged upon solidification of the metal. Direct combination of silver with chlorine, bromine, and iodine at ordinary temperatures, and with sulphur and phosphorus at a moderate heat. Tarnishing of silver by exposure to sulphuretted vapours and liquids. Its resistance to action of hydrochloric acid, but reaction with hydriodic acid to form silver-iodide (soluble in excess of acid) and evolve hydrogen. Solubility of silver in diluted nitric acid with evolution of nitric oxide, and in heated strong sulphuric acid with evolution of sulphurous anhydride. Its solution in cyanide of potassium solution under exposure to air, and similar behaviour with moistened common salt:

$$4NaCl + Ag_2 + H_2O + O = 2(NaCl.AgCl) + 2NaHO$$

Indifference of metallic silver to fused hydrates, carbonates, and nitrates of alkali-metal. Its combination with mercury to form crystalline amalgam.

Fluoride, AgF; a soluble salt, made by dissolving silver oxide or carbonate in aqueous hydrofluoric acid.

Chloride, $AgCl$; found native, crystallised in cubes or octahedrons, and in semi-vitreous sectile masses. Its production by direct combination of silver and halogen. Its usual formation by precipitating solution of silver nitrate with chloride of hydrogen or metal. Insolubility of resulting white precipitate in nitric acid. Ready fusibility of dry chloride of silver, and its subsequent solidification into horny solid. Its volatility at a stronger heat.

Solubility, to some extent, of silver chloride in strong solutions of chloride of hydrogen or basylous metal, to form double chlorides. Its solubility in aqueous ammonia, and deposition therefrom in crystalline state by volatilisation of ammonia. Its solubility in solutions of hyposulphite of sodium and cyanide of potassium, with formation of double salts:

$$AgCl + 2KCN = KCl + KAg(CN)_2$$
$$AgCl + NaHSO_2 = NaCl + NaAg(HSO_2)_2$$

Its decomposition by ebullition with strong caustic potash:

$$2AgCl + 2KHO = 2KCl + Ag_2O + H_2O$$

Its reduction, in moist way, by zinc; and by fusion with lime or alkali-carbonate. Its irreducibility by charcoal alone. Its decomposition by exposure to light, with formation of slate-coloured subchloride and evolution of chlorine.* Decomposition of the sub-chloride by hyposulphite of sodium to form insoluble silver-sulphide.

Bromide, $AgBr$; made by decomposing nitrate of silver with bromide of potassium. A yellowish-white precipitate, insoluble in nitric acid, soluble in large quantity of ammonia, and, as double salt, in solutions of alkali-bromide, cyanide, and hyposulphite. Its fusion below a red heat, and decomposition by chlorine with extrusion of bromine.

Iodide, AgI; usually made by decomposing nitrate ofsilver with iodide of potassium. A pale yellow precipitate, insoluble in nitric acid, and insoluble in, but turned white by ammonia. Its other properties similar to those of the bromide. Its solubility not only in potassium iodide but also to a considerable extent in hydriodic acid, with formation of crystalline double salt $AgI.HI$. Solubility of metallic silver in hydriodic acid, with liberation of hydrogen and gradual deposition of silver iodide in six-sided prisms:

$$Ag_2 + 2HI = H_2 + 2AgI$$

Oxide, Ag_2O; made by adding nitrate of silver to excess of caustic potash or soda. Precipitate, as first produced, apparently the hydrate $AgHO$, convertible into the oxide spontaneously, or by heat of 60°:

$$2AgNO_3 + 2KHO = 2KNO_3 + 2AgHO \quad (\text{or } Ag_2O + H_2O)$$

Silver oxide a powerful base, slightly soluble in pure water to form a feebly alkaline liquid, and uniting with even the strongest acids to form perfectly neutral salts, some of them isomorphous with those of sodium. Ready reducibility of silver oxide, partially

by light, completely by more basylous metals, by hydrogen at 100°, and *per se* at a red heat. Solubility of precipitated silver oxide in ammonia, and deposition from resulting solution, on its exposure to air, of fulminating silver in micaceous scales. Same compound formed by digesting silver oxide in ammonia, precipitating ammoniacal solutions of silver salts with potash, &c. A violently explosive body, probably the nitride Ag_3N. Its immediate decomposition by acids, with formation of silver and ammonia salts:

$$Ag_3N \quad + \quad 4HCl \quad = \quad 3AgCl \quad + \quad NH_3.HCl$$

Existence of unstable silver suboxide Ag_4O, and of a peroxide Ag_2O_2. The latter formed in dark grey needles, by electrolytic decomposition of nitrate of silver solution. Its reactions with acids and ammonia to evolve oxygen and nitrogen respectively.

Sulphide, Ag_2S; found native as silver glance, either in massive state or crystallised in cubes and octahedrons. Familiar tarnishing of silver by its exposure to sulphuretted vapours, contact with sulphuretted animal matters, &c. Its immediate blackening when touched with a soluble sulphide. Formation of silver sulphide by decomposing silver solutions with sulphuretted hydrogen, or by fusing the metal with excess of sulphur. Sulphide, after fusion, a soft somewhat malleable solid, non-conductive of electricity in the cold, but becoming conductive at a moderate heat. Its undecomposibility by heat alone, but decomposition when heated in a current of air, with production of metal and sulphurous anhydride:

$$Ag_2S \quad + \quad O_2 \quad = \quad Ag_2 \quad + \quad SO_2$$

Its decomposition by ignition with more basylous metals; and by treatment with strong acids at moderate heat.

Silver sulphide a well-characterised sulphur base, combining by way of fusion with more negative metal sulphides, to form sulpho-salts, some of them also found native, as red silver:

$$3Ag_2S \quad + \quad Sb_2S_3 \quad = \quad 2Ag_3SbS_3$$

Frequent isomorphous replacements of silver sulphide and cuprous sulphide by one another in native sulpho-salts.

Nitrate, $AgNO_3$; made by dissolving silver in moderately strong nitric acid, and evaporating down:

$$8HNO_3 + Ag_6 = 6AgNO_3 + 4H_2O + 2NO$$

Copper, if present, removable by ebullition of solution with precipitated silver oxide, or by continued heating of fused salt. Ready crystallisation of the nitrate in white anhydrous tables. Its fusion unchanged at a moderate heat, and solidification as lunar caustic. Its decomposition at a stronger heat, with intermediate production of some nitrite, to leave metallic silver. Its free solubility in water, and in boiling alcohol. Unalterability of silver nitrate by light, in absence of organic matter. Its well-known production of black stains on various organic tissues exposed to light. Its direct combination with ammonia. Production of crystals $2NH_3.AgNO_3$, by passage of ammonia gas through concentrated nitrate of silver solution.

Sulphate, Ag_2SO_4; made by boiling metallic silver in strong sulphuric acid:

$$2H_2SO_4 + Ag_2 = Ag_2SO_4 + 2H_2O + SO_2$$

Dissolution of the sulphate in excess of acid, and its precipitation therefrom on dilution. Its occurrence in small anhydrous prismatic crystals, isomorphous with those of anhydrous sodium sulphate. Its ready fusibility by heat, and undecomposibility save at a very high temperature. Its absorption of ammonia, and formation of crystalline compound $4NH_3.Ag_2SO_4$.

Phosphate, Ag_3PO_4. A yellow precipitate formed by addition of sodium phosphate to silver nitrate:

$$Na_2HPO_4 + 3AgNO_3 = Ag_3PO_4 + 2NaNO_3 + HNO_3$$

Its ready solubility in ammonia and dilute nitric acid, alteration by exposure to light, and fusibility at a red heat.

Silver allied to alkali-metals by the isomorphism of its sulphate with that of sodium, and of its alumino-sulphate with ordinary

alum; by the solubility, though to very slight extent, and alkaline reaction of its hydrate; and by the perfect neutrality, the ready fusibility, and the relatively great stability at high temperature of its salts. Silver distinguished from alkali-metals, by permanency of the metal, easy reducibility of its salts, and insolubility of its chloride, iodide, and sulphide. Silver compounds recognised by their precipitation from solution by hydrochloric and sulphydric acids, and by their ready reduction to metallic state before the blowpipe.

(63.) Gold.

Gold found to greater or less amount in many parts of the world, nowadays most abundantly in Australia and California, always in reguline state, alloyed with more or less silver, and frequently with small quantities of other metals. Its occurrence in cubes and octahedrons; in irregular grains, nodules, and masses; and in filaments, laminæ, &c., distributed in quartzose and slaty rocks, in detritus of such rocks, and in river sands. Association of gold with iron and copper pyrites, &c. Gold ex- (1) tracted from gravel and sand by simple washing with water; from (2) auriferous quartz, by crushing and amalgamation; from auriferous (3) pyrites, by crushing or roasting, washing and amalgamation. Mercury in excess pressed out, and that of residual solid amalgam distilled off. Amalgamation process much facilitated by admixture of mercury with small proportion of sodium-amalgam.

In separation of gold from silver, proportion of gold, when exceeding 20 per cent., reduced to that amount by fusion with additional silver (quartation). Alloy then granulated and boiled in sulphuric acid, or digested in nitric acid, so as to dissolve silver and leave gold (parting), afterwards melted into ingots. Sulphuric acid process generally preferable, but impeded by presence of much copper, through insolubility of its sulphate in sulphuric acid. Silver thrown down from the sulphate as a metallic deposit upon copper plates, and from the nitrate as chloride by addition of common salt. Gold also freed from silver, copper, &c.,

by passage of chlorine gas through the melted metal, covered with layer of borax. Fine gold obtained by precipitating the terchloride with solution of ferrous sulphate, boiling precipitate of reduced metal several times with hydrochloric acid, and finally melting it with flux of acid-sulphate of potassium.

Gold, a highly lustrous, orange-yellow metal, of sp. gr. 19·34, rather less heavy than platinum, nearly as soft as lead, nearly as ductile as silver, and of higher malleability than any other metal. Well marked translucency of gold in thin films. Colour of the transmitted light green, but, upon rendering the film non-lustrous by heat, ruby-red. Existence of finely divided gold in ruby glass, and in the red liquids formed by reducing gold solutions with phosphorus. Conductivity of gold for heat and electricity very perfect, but inferior to that of silver and copper. Its melting point, 1250°, higher than that of copper, and much higher than that of silver. Considerable shrinking of the metal upon solidification. Its volatilisation at very high temperatures, as that of the oxyhydrogen blowpipe.

Non-oxidisability of gold by air or oxygen, either at ordinary temperatures or under strong ignition. Its insolubility in sulphuric, nitric, and hydrochloric acids, and resistance to action of fused caustic alkalis. Its solubility in aqua-regia and other solutions of chlorine. Its solubility also in aqueous cyanide of potassium, under exposure to air:

$$4KCy + Au_2 + H_2O + O = 2KAuCy_2 + 2KHO$$

Existence of various gold alloys. Standard for coin, 11 parts gold with 1 copper. Its specific gravity 17·157, instead of mean 18·47. Best jeweller's gold, 18 parts gold to 6 silver-copper (18 carat). Alloys harder and more fusible than pure metal.

Considerable solubility of gold in mercury, especially when heated. Separation of pasty amalgam, by straining away of excess of mercury through chamois leather. Existence of well-defined crystalline amalgams, Hg_4Au_2 and Hg_6Au_2, obtainable from pasty amalgam by pressure, action of nitric acid, &c.

Gilding of porcelain, by means of gold powder painted on

Articles then fired and burnished. Gilding of wood, paint, silk, leather, &c. by gold leaf. Gilding of copper, silver, bronze, &c. by gold amalgam. Articles heated so as to drive off mercury and leave film of gold. Gilding of copper and bronze trinkets by their immersion in boiling solution of mixed gold terchloride and potassium acid-carbonate. Electro-gilding by means of double cyanide of gold and potassium dissolved in excess of cyanide of potassium solution.

Existence of two classes of gold salts; aurous, typified by the chloride AuCl, and auric, typified by the chloride $AuCl_3$.

AUROUS COMPOUNDS.

Aurous chloride, AuCl; made by gently heating residue of evaporated auric chloride solution. A yellowish-white, saline mass, permanent when dry, insoluble in cold water, quickly decomposed by boiling, and slowly by cold water, into metallic gold and auric chloride:

$$3AuCl = Au_2 + AuCl_3$$

Its decomposition by ignition into metallic gold and chlorine.

Aurous iodide, AuI; produced, with separation of iodine, by action of hydriodic acid upon auric oxide, or of iodide of potassium on excess of auric chloride:

$$AuCl_3 + 3KI = AuI + I_2 + 3KCl$$

A yellow crystalline powder, insoluble in cold, sparingly soluble in hot water.

Aurous cyanide, AuCy; obtained by boiling the potassio-cyanide in hydrochloric acid. Yellow crystalline powder, insoluble in water, and very stable. Its decomposition by heat into gold and cyanogen. Its solubility in ammonia, cyanide of potassium, and hyposulphite of sodium. Double potassium cyanide, KCy.AuCy or $KAuCy_2$, made by dissolving precipitated auric oxide, &c., in boiling cyanide of potassium solution. Deposition of salt on cooling, in colourless rhomboïdal octahedrons

or scales. Its permanency in air, and moderate solubility in water. Its use in processes of gilding and electro-gilding.

Aurous oxide, Au_2O; made by decomposing aurous chloride with cold solution of potash. A green powder, sparingly soluble in excess of potash, with gradual conversion into gold and auric oxide.

Aurous sulphide, Au_2S; made by passing sulphuretted hydrogen through boiling solution of auric chloride. A dark brown or black precipitate, soluble in aqueous alkali sulphides. The double sodium sulphide $NaAuS.4Aq$, also made by fusing together gold, sulphur, and sulphide of sodium, digesting product in water, filtering solution out of access of air, and evaporating filtrate in vacuo over oil of vitriol. Its deposition in yellow prismatic crystals, soluble in water and alcohol.

Aurous sodium hyposulphite $Na_3Au(HSO_2)_4$, made by mixing concentrated solutions of auric chloride and sodium hyposulphite, precipitating mixed liquid with alcohol, dissolving precipitate in water, and reprecipitating it by alcohol. Colourless needles, dissolving easily in water and but sparingly in alcohol.

Powder of Cassius, made by adding solution of stannous chloride, preferably containing some stannic chloride, to—or by digesting metallic tin in—dilute solution of auric chloride, freed from any excess of acid. Production of a slowly subsiding purple powder, appearing brown after subsidence. Solubility of the moist precipitate in ammonia to form a deep crimson liquid, depositing powder of Cassius and becoming colourless, slowly on volatilisation of, speedily on neutralisation of, its ammonia. Insolubility of powder of Cassius in fixed alkalis. The dried compound a purple-blue powder, not changing in appearance, and suffering only some loss of water, on being heated to redness. Chemical nature of powder of Cassius unascertained, supposed to be expressed by formula $Au_2O.Sn_2O_3$. The product of its ignition composed of finely divided gold and stannic oxide, $Au_2 + 2SnO_2$. A variety of powder of Cassius obtainable by acting with nitric acid on alloy of tin and gold with much silver, so as to dissolve away silver and leave mixed gold and stannic

acid in finely divided state. Use of powder of Cassius for production of ruby glass, and in porcelain painting as a rose-purple pigment.

AURIC COMPOUNDS.

Chloride, $AuCl_3$; obtained by evaporating down solution of gold in *aqua-regia* with excess of hydrochloric acid, heating the residue until its evolution of chlorine is very perceptible, extracting with boiling water, and evaporating resultant solution to dryness. A dark red crystalline mass, deliquescent in air, very soluble in water to form a deep red solution, and soluble also in ether and alcohol. Its combination with the chlorides of hydrogen, alkali-metal, ammonium, &c., to form yellow crystallisable salts. The hydrogen chloride $HCl.AuCl_3$, or $HAuCl_4$, produced by dissolving gold in *aqua-regia*, and evaporating solution with excess of hydrochloric acid. Its crystallisation in long yellow needles, permanent in dry but deliquescent in moist air. Ordinary aqueous terchloride of gold in reality a solution of this salt. Reduction of its gold to metallic state by phosphorus, sulphurous acid, antimonious chloride, ferrous sulphate, oxalic acid, &c., and partially by exposure to sunlight. Purple staining of most organic tissues, wetted with chloride of gold solution and exposed to sunlight. Formation of ruby-red liquid by addition of disulphide of carbon solution of phosphorus to dilute solution of gold terchloride. Colour (like that of ruby glass) due to finely divided metallic gold, deposited in course of some months, or in a few hours after addition of common salt, leaving colourless supernatant liquid. Usual reduction of gold by ferrous sulphate or oxalic acid, gradually at ordinary temperatures, rapidly at boiling heat. Its separation as a finely divided, slowly subsiding precipitate, appearing blue or purplish when viewed by transmitted light:

$$2AuCl_3 + 6FeSO_4 = Au_2 + Fe_2Cl_6 + 2Fe_2(SO_4)_3$$
$$2AuCl_3 + 3H_2C_2O_4 = Au_2 + 6HCl + 6CO_2$$

Precipitability of gold terchloride by sulphuretted hydrogen, as

intermediate sulphide, $Au_2S.Au_2S_3$ or Au_4S_4, from cold dilute solutions, and as aurous sulphide, Au_2S, from stronger solutions at boiling heat. Its non-precipitability by potash and its carbonate, save in presence of organic matter. Its precipitability by cyanide of potassium, as aurous cyanide; by ammonia and its carbonate, as fulminating gold; and by stannous chloride, as purple of Cassius. Its combinations with alkali-metal chlorides, as $NaAuCl_4.2Aq$, $NH_4AuCl_4.4Aq$, &c., obtained in crystalline state by evaporating down solutions of the mixed chlorides.

Oxide, Au_2O_3; and hydrate or acid, $HAuO_2 = \frac{1}{2}(H_2O.Au_2O_3)$. Compound produced, in form of hydrate, by digesting magnesia in auric chloride, treating well-washed deposit of magnesium aurate with dilute nitric acid, and drying residue over oil of vitriol. A reddish brown powder, becoming anhydrous below 100°, undergoing partial reduction even at 100°, and speedy complete reduction by further heating or on exposure to sunlight. Its dissolution in concentrated nitric and sulphuric acids, and precipitation unchanged on dilution of acid liquids. Its solubility in hydrochloric acid, with production of auric chloride. Its reactions with alkalis (*vide infra*). Its acidulous character shown by its partial expulsion of hydrochloric and sulphuric acids from their potassium and ammonium salts.

Potassium aurate, $K_2O.Au_2O_3 = 2KAuO_2$; made by dissolving auric oxide in slight excess of pure potash, and evaporating down, ultimately in vacuo. Colourless, or slightly yellow, hydrated needles, $KAuO_2.3Aq$, dissolving freely in water to form a strongly alkaline liquid, reducible by ebullition, and by contact with most organic tissues. Its precipitation of insoluble aurates from solutions of most metallic salts. Aurate of potassium also formed in solution by digesting auric oxide in carbonate, or even in chloride of potassium at a gentle heat:

$$HAuO_2 \;+\; KCl \;=\; KAuO_2 \;+\; HCl$$

Fulminating gold, made by precipitating auric chloride with excess of ammonia and thoroughly washing the precipitate, at first with boiling dilute potash and afterwards with water. Same

or allied compound formed by digesting auric oxide in aqueous ammonia, or in solution of carbonate, sulphate, or chloride of ammonium, with liberation from respective salts of carbonic, sulphuric, and hydrochloric acids. An olive-brown powder, stable when moist, extremely explosive when dry. Its composition unascertained, but usually represented by formula $4NH_3.Au_2O_3.H_2O$. Compound probably an amidogen representative of auric oxide or hydrate, $\overset{'''}{Au}_2O(H_2N')_4$ or $H\overset{'''}{Au}O(H_2N')_2$.

$$HAuO_2 \quad + \quad 2H_3N \quad - \quad H_2O \quad = \quad HAuO(H_2N)_2$$

Production of complex salt, $K_3\overset{'''}{Au}(SO_3)_4.x Aq$, in beautiful yellow needles, on adding neutral sulphite of potassium drop by drop to alkaline solution of the aurate. Its stability in alkaline solution, but decomposition by pure water, with reduction of gold to metallic state.

Gold allied to silver by the constitution and habit of its several monad compounds, and especially by their tendency to form soluble crystallisable double salts of alkali-metal. Distinguished from silver by its resistance to oxidation and the action of acids (nobility), and by its formation of triad compounds. Relation of gold to silver, parallel with that of platinum to palladium (?). Recognition of dissolved gold by its reduction to reguline state on ebullition with oxalic acid or ferrous sulphate; and by its furnishing purple of Cassius with stannous chloride.

CHAPTER VII.

(64.) Magnesium Elements.

Calcium, Strontium, Barium.

Beryllium—Magnesium, Zinc, Cadmium—Mercury.

Malleable conductive metals, characterised by property of replacing the hydrogen of hydrochloric acid, in proportion of one atom of metal to two atoms of hydrogen, with formation of fusible chlorides, having the general formula $\overset{''}{M}Cl_2$ and atomic heat $6{\cdot}2 \times 3 = 18{\cdot}6$. Division of metals into an alkaline-earth and a reguline sub-group. Symbols and atomic weights:

Be	Beryllium	9					
Mg	Magnesium	24		Ca	Calcium	40	
Zn	Zinc	65	67	Sr	Strontium	87·5	88·1
Cd	Cadmium	112		Ba	Barium	137	
Hg	Mercury	200					

Calcium, strontium, and barium, the most basylous of diad metals. Their want of volatility (?), and of permanency in air. Increase of basylity with increase of atomic weight, and other gradational differences, between successive members of this sub-group. Their parallelism with the potassium-metals.

Beryllium (?), magnesium, zinc, cadmium, and mercury, readily volatile metals, permanent in air. Vapour-densities of cadmium and mercury found to be the halves of their respective atomic weights. Consequent identity of atomic and molecular proportions of the two metals, alike represented by symbols Cd and Hg respectively. Correspondence of molecules of vaporous zinc

ethide $ZnEt_2$, mercuric ethide $HgEt_2$, and mercuric chloride $HgCl_2$, to normal 2-volume standard. Association of magnesium, zinc, and cadmium with one another more decided than their association with beryllium and mercury, but less decided than mutual association of the alkaline-earth metals. Approximation in character between compounds of calcium and magnesium.

From analogy of certain of its monad compounds to corresponding compounds of barium, the tetra-diad metal lead, symbol Pb, atomic weight 207, conveniently considered in association with the alkaline-earth metals. Relation of tetra-diad lead to calcium and barium, similar to that of tris-monad metal thallium to potassium and cæsium.

(65.) Calcium, Strontium, Barium.

Extensive distribution of calcium in form of carbonate $CaCO_3$, as chalk, limestone, marble, calc-spar, &c., and of double carbonate, as magnesian limestone or dolomite. Its abundance moreover in forms of selenite, gypsum, or alabaster $CaSO_4.2H_2O$; apatite $Ca_5(PO_4)_3F$, fluor-spar CaF_2, and labradore $CaAl_2O_4.Si_3O_6$. Its existence also in many other mineral species, as for example in anhydrite $CaSO_4$, and certain hydrated alumino-silicates known as zeolites. Occurrence of dissolved chloride, acid-carbonate, and sulphate of calcium in sea-, river-, spring-, and mineral waters, especially in those known as calcareous. Presence of carbonate and phosphate of calcium in vegetable ashes. Their existence also in the animal kingdom, both in the soft tissues, and concentrated in shell, coral, bone, &c.

Principal occurrence of strontium in form of cælestine $SrSO_4$, and strontianite $SrCO_3$; and of barium in form of heavy-spar $BaSO_4$, and witherite $BaCO_3$. Carbonates of calcium and barium with some carbonate of strontium met with in form of barytocalcite.

Employment of native carbonate, hydrated sulphate, fluorphosphate, and fluoride of calcium in chemical and other manu-

factures. Nearly all artificial calcium compounds obtained from the carbonate. Those of strontium and barium obtained partly from respective carbonates, but chiefly from the sulphates, after their conversion into sulphides by ignition with charcoal, &c.

Calcium, strontium, and barium, best made by electrolysis of the respective fused chlorides. Yellowish coloured, moderately hard, malleable metals, fusible at a red heat. Their immediate decomposition of water and dilute acids, with evolution of hydrogen. Their gradual oxidation in dry, and rapid oxidation in moist air. Their combustibility at a red heat without flame, showing want of volatility. Sp. gr. of calcium 1·8, of strontium 2·5, of barium about 4·0. Ready amalgamation of all three metals by mercury. Barium heavier, more coloured, less fusible, and more oxidisable than the other two metals.

COMPOUNDS WITH HALOGENS.

Fluorides. That of calcium CaF_2, found native in abundance as fluor-spar—either massive or crystallised, usually in cubes. An insoluble, fusible, frequently phosphorescent compound, decomposible by sulphuric acid at a gentle heat.

Chlorides. That of calcium $CaCl_2$, made by decomposing chlorides of hydrogen, manganese, or ammonium, with carbonate of calcium in form of marble or chalk. A fusible, deliquescent, very soluble salt. Boiling point of saturated solution 180°. Formation of transparent hydrated prisms $CaCl_2.6Aq$, by its evaporation, and of porous crystalline mass $CaCl_2.2Aq$, by further heating. Liquefaction of crystals by snow, with great absorption of heat. Constant employment of both fused anhydrous salt and porous hydrate as desiccating agents. Free solubility of calcium chloride in alcohol, and crystallisation from solution of an alcoholate $CaCl_2.4C_2H_6O$. Absorption of ammonia by calcium chloride to form compound $CaCl_2.8H_3N$. Solubility of lime in hot chloride of calcium solution to form hydrated crystalline oxichloride $Ca_2Cl(HO)_3.6Aq$, decomposible by water. Chloride of strontium $SrCl_2$, and of barium $BaCl_2$, made by dissolving the respective native car-

bonates or crude sulphides in hydrochloric acid and evaporating. That of strontium, a fusible deliquescent salt, crystallising with six atoms of water, freely soluble in water and alcohol. That of barium sometimes made by fusing the native sulphate with chloride of calcium and extracting product with water. A fusible non-deliquescent salt, soluble in water, not in absolute alcohol, and crystallising in tables with two atoms of water. General resemblance of bromides and iodides to above chlorides respectively.

COMPOUNDS WITH OXYGEN, ETC.

Oxides. That of calcium, or quicklime CaO, formed by igniting the carbonate, hydrate, or nitrate. Ordinary lime made by intermittent or continuous burning of limestone in kilns: presence of moisture advantageous. For chemical purposes, marble ignited in crucibles. A white, infusible solid, absorbing moisture and carb-anhydride from the atmosphere to form compound $Ca_2(HO)_2CO_3$. Use of quicklime as a desiccating and antiseptic agent (?).

Anhydrous strontia and baryta made by strong ignition of respective nitrates, not of hydrates or carbonates. Baryta fusible in the oxihydrogen blow-pipe. Absorption of oxygen by porous baryta at a red heat to form the peroxide BaO_2.

Hydrate of calcium, or slaked lime, $Ca(HO)_2$ or $CaO.H_2O$, a dry powder, made by slaking quicklime with cold or hot water. Reaction attended with great evolution of heat. Opaque mixture of slaked lime and water, known as milk of lime. Solubility of the hydrate in about 530 times its weight of cold water, to form an alkaline, feebly caustic liquid, much used as a test for carbonic acid. Its action on acids, salts, &c., similar to that of dilute potash or soda. Greater solubility of calcium hydrate in syrup than in water; its deposition from both solutions by increase of temperature; its production in form of six-sided prisms or tables by evaporation of lime-water in vacuo. Decomposition of calcium hydrate at a red heat into quicklime and water:

$$Ca(HO)_2 \quad = \quad CaO \quad + \quad H_2O$$

Its employment on large scale for absorption of chlorine, in manufacture of bleaching powder:

$$Ca(HO)_2 \quad + \quad Cl_2 \quad = \quad Ca(ClO)Cl \quad + \quad H_2O$$

Various other uses of slaked lime; as for softening hard waters; as a defæcant, especially of sewage; as a depilatory &c. in processes of tanning; as an agent for saponifying fats, preparing caustic alkalis, and purifying coal gas; as a manure, upon peaty or clayey soils; and, mixed with sand, for making ordinary mortar. Imperfect carbonation and silication of lime in old mortar. Presence of magnesia, alumina, silica, &c. (or clay) in hydraulic limes and cements, natural and artificial.

Slaking of strontia and baryta similar to that of lime. Greater solubility of resulting hydrates, especially barium hydrate, in water to form more caustic liquids than lime-water. Separation of hydrated crystalline hydrates $Sr(HO)_2.8Aq$, and $Ba(HO)_2.8Aq$, on cooling hot saturated solutions. Hydrate of barium sometimes made by boiling up the crude sulphide with oxide of copper, or the chloride or nitrate with strong caustic soda. Its crystallisation from resulting liquids and purification by recrystallisation. Fusibility of barium hydrate without, and of strontium hydrate with very partial, decomposition, even at a strong red heat.

Crude barium peroxide BaO_2, made by gently heating the hydrate or oxide in a current of air or oxygen, or by heating a mixture of the oxide with chlorate of potassium:

$$3BaO \quad + \quad KClO_3 \quad = \quad 3BaO_2 \quad + \quad KCl$$

Product converted into practically insoluble hydrate $BaO_2.6Aq$, by action of water. Pure compound made by dissolving the crude hydrate in excess of cold dilute hydrochloric acid, rendering solution slightly alkaline with baryta-water to precipitate any iron or alumina, filtering rapidly through linen, and adding resultant filtrate of hydrogen peroxide in excess to baryta-water:

$$H_2O_2 \quad + \quad BaH_2O_2 \quad = \quad BaO_2 \quad + \quad 2H_2O$$

Hydrated peroxide thus produced in silky plates, capable of being

washed with water, and rendered anhydrous by desiccation over oil of vitriol in vacuo. Anhydrous compound a mobile, white, magnesia-like powder.

Similar precipitates producible by action of hydrogen peroxide on lime- and strontia-water.

Barium peroxide decomposed, by strong ignition into baryta and oxygen; and by treatment with hydrochloric acid into barium chloride and peroxide of hydrogen with the cold dilute, into barium chloride and chlorine with the hot concentrated acid:

$$BaO_2 + 2HCl = H_2O_2 + BaCl_2$$
$$BaO_2 + 4HCl = 2H_2O + BaCl_2 + Cl_2$$

Sulphydrates of calcium, strontium, and barium, made by saturating solutions of the respective hydrates with sulphuretted hydrogen. Definite crystallisable compounds, corresponding in properties to alkali-metal sulphydrates. Crude sulphide of calcium produced in carbonate of sodium manufacture. Crude sulphides of strontium and barium made purposely by ignition of the sulphates with starch, charcoal, &c. Their employment for preparation of the chlorides, and other strontium and barium salts:

$$BaS + 2HCl = BaCl_2 + H_2S$$

All three sulphides insoluble in cold or tepid water, but decomposible by ebullition into soluble hydrate and sulphydrate:

$$2BaS + 2H_2O = Ba(HO)_2 + Ba(HS)_2$$

Pentasulphide of calcium produced, as a deep orange liquid, by boiling milk of lime with sulphur. Its decomposition, by exposure to air, into colourless solution of the hyposulphite:

$$CaS_5 + H_2O + O_3 = Ca(HSO_2)_2 \text{ or } CaS_2O_3.H_2O + S_3$$

Phosphide. Crude calcium phosphide, Ca_3P_2 or Ca_2P_2 (?), produced, in hard brown masses, by passing phosphorus vapour over ignited quicklime. Decomposition of product by water or dilute acids, to yield spontaneously inflammable phosphoretted hydrogen.

OXISALTS.

Nitrates. That of calcium $Ca(NO_3)_2$, made by dissolving the carbonate in dilute nitric acid. A very soluble, deliquescent salt, crystallising in prisms with 4 atoms of water. Solubility of the anhydrous and hydrated salt in alcohol. Production of calcium nitrate, in spontaneous and artificial processes of nitrification, as saltpetre-rot. Nitrates of strontium and barium, $Sr(NO_3)_2$ and $Ba(NO_3)_2$, made by dissolving the respective carbonates or crude sulphides in dilute nitric acid. Usual crystallisation of both salts in anhydrous octahedrons insoluble in alcohol. Barium nitrate much employed as a precipitant of sulphuric acid. Its moderate solubility in cold water and precipitability on addition of much nitric acid. All three nitrates decomposed by strong ignition, to leave the respective oxides.

Carbonates. Occurrence of calcium carbonate $CaCO_3$, in impure state as limestone and chalk; more pure as marble; and crystallised dimorphously as calc-spar and arragonite. Also in forms of coral, shell, &c., and as a constituent of marl. Its artificial production by decomposing solutions of nitrate or chloride of calcium with carbonate of ammonia, and gently igniting washed precipitate. Decomposition of carbonate of calcium at a full red heat into quicklime and carbanhydride. Its semi-fusion, without decomposition, when heated in close vessels. Its almost insolubility in water. Its moderate solubility in aqueous carbonic acid, to form compound $H_2Ca(CO_3)_2$ (?); and its deposition on exposure of the solution to air, or on ebullition. Occurrence of similarly dissolved carbonate of calcium, to greater or less extent, in most natural waters. Its occasional deposition in forms of stalactite, stalagmite, travertine, boiler-fur, &c. Temporary hardness of waters caused by dissolved acid-carbonate of calcium. Its precipitation as neutral carbonate by addition of lime.

Carbonates of strontium and barium, $SrCO_3$ and $BaCO_3$, precipitable from solutions of the respective metals by carbonated alkalis; and found native, in massive state, or in crystals iso-

morphous with those of calc-spar. Barium carbonate undecomposed, and that of strontium but slightly decomposed, by strong ignition. Both compounds decomposed by ignition with charcoal, to leave the respective oxides; and by ignition in a current of steam to leave the hydrates. Some amount of barium carbonate made by passing carbonic acid gas through solution of the crude sulphydrate (formed by reduction of the sulphate), and used as a substitute for lead oxide in glass manufacture:

$$BaO.CO_2 \ + \ 2SiO_2 \ = \ BaO.2SiO_2 \ + \ CO_2$$

Sulphates. Occasional occurrence of calcium sulphate $CaSO_4$, in anhydrous crystalline form, as anhydrite; and far more abundantly, combined with two atoms of water, either in massive state as gypsum and alabaster, or crystallised as selenite. A sparingly soluble salt, present in many spring waters, thence called selenitic, and deposited therefrom on evaporation, as a compact fur. Insolubility of calcium sulphate in spirit of wine. Its artificial production by precipitating dissolved calcium salts with sulphate of hydrogen or metal.

Dehydration of gypsum &c., at about 250°, with production of plaster. Rapid rehydration or setting of plaster on its admixture with water, attended by expansion and evolution of heat. Over-burnt gypsum semi-crystalline, and incapable of setting. Its fusion at a powerful heat. Production of various cements by heating gypsum with small quantities of different salts, as borax, alum, white vitriol, &c.

Sulphates of strontium and barium, $SrSO_4$ and $BaSO_4$, found native (the latter very abundantly) in massive state or crystallised isomorphously in right rhombic prisms. Both salts formed artificially, in anhydrous state, by precipitating strontium and barium solutions with sulphuric acid or other soluble sulphate. Barium sulphate quite, and that of strontium almost, insoluble in water and dilute acids. Fusibility of both salts at an intense red-heat. Their decomposition when fused with, or in freshly-precipitated state when boiled with, carbonated alkali, to yield the respective carbonates; and their decomposition when ignited with charcoal,

to yield the respective sulphides, each convertible into mixed hydrate and sulphydrate by ebullition with water:

$$BaSO_4 + C_4 = BaS + 4CO$$

Use of barium sulphate, under the name of permanent white, as a pigment; and in manufacture of paper, to give weight, and improve surface.

Phosphates. That of calcium $\overset{\prime\prime}{Ca}_3(PO_4)_2$, largely distributed in nature as coprolite, phosphorite, &c. Its occurrence in combination with chloride or fluoride of calcium as apatite, either massive or finely crystallised in hexagonal prisms:

$$3Ca_3(PO_4)_2.CaF_2 = 2Ca_5(PO_4)_3F.$$

Existence also of calcium phosphate as the chief constituent of bone-ash. Its formation as a hydrated gelatinous precipitate $Ca_3(PO_4)_2.2Aq$ (rendered anhydrous at 100°), by addition of calcium chloride to excess of sodium phosphate solution. More or less ready solubility of calcium phosphate in mineral acids, and of the precipitated phosphate even in acetic acid, to form the superphosphate $\overset{\prime\prime}{Ca}_2H_4(PO_4)_2$. Production of intermediate phosphate $\overset{\prime\prime}{Ca}_2H_2(PO_4)_2$, in semi-crystalline state, by addition of sodium phosphate to excess of calcium chloride solution. Strontium and barium phosphates known only as precipitates, closely resembling precipitated calcium phosphate.

Compounds of diad alkali-metals mostly infusible before the blowpipe, saving the chlorides, &c. Their coloration of the blowpipe flame, orange-red by calcium, crimson by strontium, and apple-green by barium. Spectrum of calcium flame characterised by bright line in the orange, and broader one in the green; that of strontium by several lines in the red and orange, with one in the blue; and that of barium by a number of lines in the green. Solutions of all three metals precipitated by aqueous carbonates, oxalates, phosphates, and sulphates—sulphate of calcium, however, being thrown down only from strong solutions or on addition of alcohol. Precipitated carbonates,

oxalates, and phosphates, soluble—sulphates insoluble—in dilute mineral acids. Barium solutions distinguished from those of the other two metals by their precipitability with silicofluoric, but not with oxalic acid, from formation in the latter case of soluble acid oxalate of barium.

(66.) LEAD.

Galena, or lead sulphide, by far the most abundant of lead ores, found in most countries of the globe, and in rocks of different geologic age. Carbonate of lead or cerusite, the sulphate or anglesite, the phosphate or pyromorphite, and the arsenate or mimetesite, occasionally worked. Very many other lead compounds met with as native minerals.

Dressed galena, with a little lime, roasted in current of air, at a gentle heat, in reverberatory furnace. Consequent conversion of some lead sulphide PbS, partly into oxide PbO, and partly into sulphate $PbSO_4$. Furnace then closed, and temperature raised so as to set up the following reactions:

$$2PbO + PbS = 3Pb + SO_2$$
$$PbSO_4 + PbS = 2Pb + 2SO_2$$

Some subsulphide of lead Pb_2S, also formed as a fusible matt, flowing out with the metal and furnaced with the next charge. Further yield of lead by heating residues, scoriæ, &c., with coke or charcoal, usually after addition of lime. Other modes of smelting also employed. Galena, whether or not first roasted, sometimes reduced by granulated or scrap iron, and sometimes by coal, peat, or other fuel, in blast furnaces, reverberatory furnaces, hearth furnaces, &c.

Calcination or improving process. Crude lead often hard through presence of antimony. Such lead kept melted in cast-iron pan, heated by reverberatory furnace, until rendered soft, through preferential oxidation of the antimony, with however much oxidation of the lead, into *dross*.

Desilvering process. Presence of more or less silver in nearly all lead smelted from galena. Five tons or so of argentiferous

lead melted in the centre one of a row of some eight or nine cast-iron pots, having separate fires. On slow cooling, granular crystals of partly desilvered lead transferred by perforated iron ladles to next pot on the right hand; and residual more fusible silver alloys, forming about one-fifth of original charge, tranferred to next pot on the left hand. Process repeated, with fresh lead in centre pot, and with the more or less desilvered and persilvered contents of pots on either side. Final discharge of desilvered lead from extreme right-hand pot, and of rich silver alloy (sometimes containing 300 ounces of silver in the ton) from pot on the left hand.

Cupellation. Above silver alloys heated by reverberatory flame on hearth or cupel, made by compressing fine bone-earth slightly moistened with solution of pearlash. Blast of air caused to play upon the melted metal, so as to transform the constituent lead into its oxide or litharge, run off or absorbed, and to leave pure silver on the cupel. Process frequently conducted at two stages. Litharge from first stage either sold or reduced; that from latter stage being argentiferous, together with that absorbed in the cupels, always reduced by ignition with powdered coal or anthracite, and the resulting metal again treated as above.

Assay and refining of the noble metals by cupellation of their lead-alloys.

Lead a bluish-grey metal, of such extreme softness as to be scratched by the nail, and to leave a streak upon paper. Its moderate malleability, inferior ductility, and very feeble tenacity. Its sp. gr. 11·36, and melting point 325°. Shrinking of the metal on solidification. Its capability of being crystallised by way of fusion in cubes or octahedrons, though with difficulty. Its considerable volatilisation at a full red heat.

Freshly cut surface of lead at first lustrous, but quickly tarnished. Spongy lead, as obtained by ignition of the tartrate, pyrophoric. Unalterability of bright lead in perfectly dry air, and also in air-free water. Its rapid corrosion by air and water jointly, with formation of soluble lead hydrate, afterwards precipitated in scales as the hydrate-carbonate, $Pb_2(HO)_2CO_3$. Action of water on lead increased by presence of nitrates and chlorides,

reduced to zero by presence of carbonates, sulphates, and phosphates. Rapid oxidation of molten lead, at high temperatures, into litharge PbO, convertible into minium, or red lead, Pb_3O_4, by further oxidation. Lead readily soluble in dilute nitric acid, with evolution of nitric oxide. Its resistance to action of hydrochloric and sulphuric acids (both strong and dilute) very considerable, even at boiling heat, and complete at ordinary temperatures. But attackability of lead by weakest acids, as the acetic and carbonic, in presence of air and moisture.

Lead-alloys. Shot metal, an alloy of lead with small proportion of arsenic. Type metal, an alloy of lead with antimony, or with antimony and tin. Metal for permanent pencils, an alloy of lead with bismuth. Pewter and solder, alloys of lead and tin. Occasional presence of bismuth in easily fusible solder.

Formation by lead of two series of compounds. Series of tetrad or plumbic compounds, typified by plumbic ethide $PbEt_4$, and plumbic oxide PbO_2. Series of diad, plumbous, or ordinary lead compounds, typified by the chloride $PbCl_2$, and oxide PbO. Characteristic formation by lead of basic or hydroxy- series of plumbous salts, and of basic, or oxy- or hydroxy- series of diplumbous salts &c.:

$PbCl_2$	Pb_2OCl_2 and	$Pb_3O_2Cl_2$
$Pb(HO)_2$	$Pb_2O(HO)_2$	,,
$PbCl.HO$	$Pb_2OCl.HO$	,,
$Pb(NO_2)_2$	,,	,,
$Pb(NO_2)HO$	$Pb_2O(NO_2)HO$	$Pb_2(NO_2)NO_3(HO)_2$
$Pb(NO_3)_2$	$Pb_2O(NO_3)_2$	,,
$Pb(NO_3)HO$	,,	,,
$PbCO_3$	$Pb_2CO_3(HO)_2$ and	$Pb_3(CO_3)_2(HO)_2$

PLUMBOUS SALTS.

Chloride, $PbCl_2$; made by precipitating solution of acetate or nitrate of lead with hydrochloric acid. A heavy white precipitate, very sparingly soluble in cold, moderately soluble in hot water, and still more soluble in hot hydrochloric acid. Its deposi-

tion on cooling of solutions, in brilliant white needles. Its fusion on gentle, and volatilisation on strong ignition. Fused chloride of lead a semi-transparent sectile mass. Its conversion into the oxichloride Pb_2OCl_2, by ignition in a current of air. Same compound found native as matlockite, and produced on large scale, as Pattinson's white lead, by precipitating hot solution of lead chloride (made by dissolving galena in concentrated hydrochloric acid) with exact sufficiency of lime-water:

$$CaO.H_2O + 2PbCl_2 = CaCl_2 + H_2O + Pb_2OCl_2$$

The oxichloride $Pb_3O_2Cl_2$, found native as mendipite. Another oxichloride $Pb_8O_7Cl_2$, known as Turner's patent yellow, made by heating litharge with sal-ammoniac.

Iodide, PbI_2; thrown down from solution of nitrate or acetate of lead by iodide of potassium, as a bright yellow precipitate, almost insoluble in cold, sparingly soluble in boiling water, and deposited on cooling of solution in brilliant golden spangles. Its formation of double salts with alkali-metal iodides, and of several oxy-iodides.

Hydrate, $Pb(HO)_2$; known only in aqueous solution, formed by digesting clean lead in pure water, subjected to a current of decarbonated air. Formation of colourless liquid, containing only $\frac{1}{10000}$ part of lead hydrate. Its faint sweetish taste, decided alkaline reaction, and absorption of carbonic acid from the air to yield a precipitate of basic carbonate. The oxy-hydrate $Pb_2O(HO)_2$, thrown down as a white precipitate, on treating nitrate or acetate of lead with slight excess of caustic alkali. Its sparing solubility in water in form of the hydrate, dehydration by heat or on exposure to sunlight, ready absorption of carbonic acid, and dissolution in excess of fixed caustic alkali or alkaline earth.

Oxide, PbO; formed on large scale by heating lead in a current of air. Production of unfused oxide in form of a dull-yellow powder, known as massicot. Production, at somewhat higher temperature, of yellowish scaly mass of fused oxide, known as litharge of silver; and, at still higher temperature, of reddish scaly mass, known as litharge of gold, or simply as litharge. Colour further heightened by occasional presence in the litharge

of some red lead. Temporary darkening in colour of lead oxide by heat, its fusion above a red heat, and solidification in crystalline scales. Its slight dissolution by pure water, in form of the hydrate. Its action as a powerful base; in its moist state absorbing carbonic acid from the air, liberating ammonia from sal-ammoniac, and decomposing fats with formation of lead soap or plaster; and in its fused state combining with silica, alumina, &c., to produce readily fusible glasses. Its formation of normal and basic salts, many of the latter, unlike basic salts in general, soluble in water, and yielding alkaline solutions. Its dissolution, for instance, in acetic acid to form lead acetate $Pb(H_3C_2O_2)_2$, and in the produced acetate to form the acetate-hydrate $Pb(H_3C_2O_2)HO$. Solubility of lead oxide in fixed caustic alkalis, and to less extent in alkaline earths, to form compounds producible in quasi-crystalline state. Production of anhydrous lead oxide, in colourless or reddish octahedrons, by exposing solution of litharge in excess of caustic soda to the air, or by cooling strong soda solutions saturated at boiling heat with litharge.

Sulphide, PbS; found native as galena, in lustrous, dark leaden-coloured cubes or crystalline masses; producible artificially by heating lead, or its oxide or carbonate, with sulphur; and in moist way by precipitating lead salts with sulphuretted hydrogen, &c. &c. Lead sulphide fusible at a full red heat, and slightly volatile. Its oxidation, when heated in a current of air, to form mixture of lead oxide and lead sulphate. Its reactions with lead oxide and sulphate, at high temperatures, to furnish metallic lead. Its reduction also by ignition with ferric oxide, deficit of nitre, carbonated alkali, lime, metallic iron, &c.:

$$PbS + O_2 = Pb + SO_2$$
$$PbS + Fe = Pb + FeS$$

Lead sulphide indifferent to cold, but moderately soluble in heated hydrochloric acid, with evolution of sulphuretted hydrogen. Its conversion into lead sulphate, when boiled with nitric or nitro-muriatic acid. Action of lead sulphide as a sulpho-base, in zinkenite $PbS.Sb_2S_3$ or $Pb(SbS_2)_2$, in boulangerite $3PbS.Sb_2S_3$ or $Pb_3(SbS_3)_2$, &c.

Evolution of sulphur from lead sulphide, strongly heated in close vessels, to leave the subsulphide Pb_2S. Same compound formed on large scale as a fusible matt, in lead smelting, by incomplete reduction of a portion of galena. Subsulphide more fusible than galena, unaltered by strong ignition, but decomposing when heated just short of its melting point into fused metallic lead and unfused lead sulphide.

Formation, on treating acid solution of lead chloride with sulphuretted hydrogen, of an intermediate bright red precipitate of lead sulpho-chloride Pb_2SCl_2, convertible into the black sulphide, Pb_2S_2 or $2PbS$, by excess of sulphuretted hydrogen.

Nitrate, $Pb(NO_3)_2$; made by dissolving lead or litharge in dilute nitric acid, and evaporating down. Its crystallisation in anhydrous regular octahedrons, usually somewhat opaque. Its decomposition by heat into lead oxide, nitric peroxide, and oxygen. The nitrate-hydrate $Pb(NO_3)HO$, made by treating solution of the nitrate with deficit of ammonia, or, preferably, by boiling it with litharge. The nitrate-oxide $Pb_2O(NO_3)_2$, sometimes produced instead. Both salts soluble and crystalline.

Nitrites. Solution of one atom of lead in one atom of lead nitrate to form the nitrate-nitrite $Pb_2(NO_3)NO_2(HO)_2$, crystallising in yellow plates (Peligot). The nitrite-hydrate, $Pb(NO_2)HO$, formed by boiling solution of the above salt for a short time with metallic lead. Its crystallisation in golden yellow needles (Bromeis). Diplumbous nitrite-hydrate $Pb_2O(NO_2)HO$, made by boiling a dilute solution of the nitrate, or of either intermediate salt, for a long time with excess of lead. Its crystallisation in flesh-red needles, but sparingly soluble even in hot water (Berzelius, Peligot). The normal nitrite $Pb(NO_2)_2$, producible by treating solutions of the basic nitrites with carbonic acid.

Carbonate, $PbCO_3$; found native as cerusite, in crystals isomorphous with those of witherite, and in fibrous masses. Producible as a white precipitate on addition of lead nitrate or acetate to excess of cold dilute solution of alkali-carbonate. Carbonate-hydrate $Pb_2CO_3(HO)_2$, formed in beautiful silky needles by joint action of carbonic acid, air, and water on

metallic lead. Another carbonate-hydrate $Pb_3(CO_3)_2(HO)_2$, procured on large scale as white lead. Cast gratings of pure lead exposed to air, moisture, vapour of vinegar, and carbonic acid gas, the latter generated by decay of spent tan surrounding the gratings and vinegar pots. Gradual conversion, by small quantity of vinegar, of large quantity of lead into basic acetate, decomposed, *pari passu*, into basic carbonate by excess of carbonic acid. White lead, of similar character and composition, formed by exposing litharge, moistened with acetate of lead solution, to carbonic acid gas furnished by the combustion of coke. White lead prepared by either process devoid of crystalline character, and very valuable as a pigment, from its great opacity. Same compound producible by precipitating solution of basic lead acetate with current of carbonic acid, but in semi-crystalline state, and of little value as a pigment. The different carbonates of lead insoluble in water, sparingly soluble in aqueous carbonic acid, blackened by sulphydric acid and alkali-sulphides, readily soluble in dilute nitric and acetic acids with effervescence, and soluble also in potash and soda. Their decomposition by heat, with evolution of carbonic acid or anhydride, to leave a residue of lead oxide.

Sulphate, $PbSO_4$; found native as anglesite, in crystals isomorphous with those of heavy spar; and formed by precipitating lead acetate or nitrate with sulphuric acid or any soluble sulphate. Its insolubility in water, solubility in acetate of ammonium solution with formation of double salt, in caustic potash and soda, in boiling hydrochloric acid with formation of lead chloride crystallising out upon cooling, and to slight extent in strong nitric and sulphuric acids. Its unalterability by mere ignition, but ready reducibility by ignition with carbon or carbonaceous gases, to the state of lead oxide, metallic lead, or lead sulphide, according to circumstances. Existence of native lead sulphate-carbonates, as lanarkite $Pb_2SO_4(CO_3)$, and lead-hillite $Pb_4SO_4(CO_3)_3$.

Phosphate, $Pb_3(PO_4)_2$, and chlorophosphate or polymorphite $Pb_5(PO_4)_3Cl$, found native, in yellow hexagonal prisms isomor-

phous with apatite $Ca_5(PO_4)_3F$, with mimetine $Pb_5(AsO_4)_3Cl$, and with vanadite $Pb_5(VO_4)_3Cl$. Lead phosphate or orthophosphate $Pb_3(PO_4)_2$, pyrophosphate $Pb_2P_2O_7$, and metaphosphate $Pb(PO_3)_2$, thrown down from lead acetate by orthophosphate, pyrophosphate, and metaphosphate of sodium respectively, as white precipitates decomposible by sulphuretted hydrogen to yield the several phosphoric acids:

$$Pb_3(PO_4)_2 \quad + \quad 3H_2S \quad = \quad 2H_3PO_4 \quad + \quad 3PbS$$

The different lead phosphates, readily fusible compounds soluble in dilute nitric acid.

PLUMBIC COMPOUNDS.

Chloride, $PbCl_4$; made by treating peroxide of lead with cold aqueous hydrochloric acid. Solution effected without effervescence. Precipitation from it of puce peroxide by hydrates, and of red persulphide by sulphydrates and sulphides. Compound producible in crystals, together with those of plumbous chloride, by evaporation in vacuo of hydrochloric acid solution. Its correspondence to lead ethide $PbEt_4$.

Oxide, PbO_2; found native in hexagonal prisms as plattnerite; producible by oxidation of plumbous oxide in many different ways; and by decomposition of intermediate oxides:

$$\begin{array}{lcl} Pb_2O_3 & \text{or} & PbO.PbO_2 \\ Pb_3O_4 & ,, & 2PbO.PbO_2 \\ Pb_4O_5 & ,, & 3PbO.PbO_2 \end{array}$$

Plumbic oxide usually made by acting on the protoxide or carbonate either with a hypochlorite—or with free chlorine, preferably in presence of alkali carbonate:

$$PbO \quad + \quad Ca\begin{cases} Cl \\ ClO \end{cases} \quad = \quad PbO_2 \quad + \quad CaCl_2$$

Or by heating red-lead with dilute nitric acid:

$$Pb_3O_4 \text{ or } 2PbO.PbO_2 + 4HNO_3 = 2H_2O + PbO_2 + 2Pb(NO_3)_2$$

Formation of plumbic oxide at the positive pole, by electrolysis of aqueous lead acetate or nitrate.

A dark puce or chocolate-brown powder, decomposing by heat into oxygen and the red oxide, and reacting with heated hydrochloric acid to furnish plumbous chloride and chlorine:

$$PbO_2 \quad + \quad 4HCl \quad = \quad 2H_2O \quad + \quad PbCl_2 \quad + \quad Cl_2$$

Its immediate combination with the nitrous and sulphurous acids or anhydrides, to form plumbous nitrate and sulphate respectively:

$$PbO_2 \quad + \quad SO_2 \quad = \quad PbSO_4$$

Its action as a powerful oxidising agent, especially upon organic substances, such as oxalic acid, tartaric acid, glucose, &c. Existence of unstable plumbic acetate, plumbic phosphate, &c.

Action of lead peroxide as an anhydride, to combine with potash, lime, plumbous oxide, &c. Potassium plumbate $K_2PbO_3.3Aq$, made by fusing plumbic oxide with caustic potash, or by boiling it for some time with strong potash, and crystallising the product from small quantity of hot water. Its deposition in white octahedrons, decomposible by excess of water or dilute acid with precipitation of plumbic oxide. Calcium plumbate $CaPbO_3$, produced as a white insoluble compound (decomposible by dilute acids as above) by digesting lead nitrate with excess of calcium hydrate and hypochlorite at a gentle heat.

Plumbous plumbates. Compound Pb_4O_5 or $3PbO.PbO_2$, an unusual form of artificial red-lead, produced occasionally in crystalline state. Its conversion into ordinary red-lead, by action of lead acetate solution:

$$Pb_4O_5 \quad = \quad PbO \quad + \quad Pb_3O_4$$

Red-lead, Pb_3O_4 or $2PbO.PbO_2$, found native as minium; produced artificially, on large scale, by oxidising unfused plumbous oxide or massicot in a reverberatory furnace, and allowing the product to cool slowly. A bright scarlet, somewhat crystalline powder, becoming darker when heated, and undergoing decomposition by strong ignition into plumbous oxide and oxygen. Its decomposition by nitric acid into plumbous nitrate and the

peroxide, and by cold dilute acetic acid into plumbous acetate and the sesquioxide:

$$Pb_3O_4 = 3PbO + O$$
$$ 2PbO + PbO_2$$
$$ PbO + Pb_2O_3$$

Action on red-lead of hydrochloric acid, in deficit, to produce plumbous chloride and plumbic oxide; and, in excess, to produce plumbous chloride and free chlorine:

$$Pb_3O_4 + 4HCl = 2H_2O + PbO_2 + 2PbCl_2$$
$$Pb_3O_4 + 8HCl = 4H_2O + 3PbCl_2 + Cl_2$$

Dissolution of red-lead in glacial acetic acid and in strong phosphoric acid, to form mixed plumbous and plumbic acetates and phosphates respectively. Separation of plumbic from plumbous salts by addition of sulphuric acid to precipitate plumbous sulphate; or, in case of the acetates, by crystallising out of sparingly soluble plumbic from more soluble plumbous acetate. Use of red-lead as an oxidising agent; in the manufacture of flint-glass; and as a pigment.

Sesquioxide, Pb_2O_3 or $PbO.PbO_2$. An occasional form of red-lead, and product of the action of dilute acetic acid upon ordinary red-lead. Compound producible by adding deficit of sodium hypochlorite to saturated solution of plumbous oxide in caustic soda, and in other ways. An orange-red, by some modes of preparation ochry-red powder, convertible by nitric acid into plumbous nitrate and plumbic oxide; and, in general, behaving similarly to ordinary red-lead.

Sulphide, PbS_2 (?); formed as a deep-red precipitate, by adding alkali sulphydrate or monosulphide to solution of plumbic acetate or chloride; or by adding alkali-persulphide to solution of plumbous acetate or nitrate. Its speedy decomposition into mixture of the black sulphide with sulphur.

Resemblance of diad lead to calcium and barium in the solubility and alkalinity of its hydrate, the basylity of its oxide, and

insolubility of its carbonate and sulphate. Isomorphism of lead-spar $PbCO_3$, with witherite $BaCO_3$; of lead-vitriol $PbSO_4$, with heavy-spar $BaSO_4$; of polymorphite $Pb_5(PO_4)_3Cl$, with apatite $Ca_5(PO_4)_3F$; of artificial lead nitrate $Pb(NO_3)_2$, with artificial barium nitrate $Ba(NO_3)_2$, &c. &c. Lead distinguished from barium by its stability in air and water separately; by its high specific gravity and atomic weight; by the precipitability of its chloride, iodide, and sulphide; by the ready reducibility of its oxides and salts; and by its marked tendency to form basic compounds.

Remarkable parallelism of tetra-diad lead, and tris-monad thallium (*q.v.*).

Recognition of lead by reducibility of its solid compounds before the blowpipe, to yield a bead of soft metal with yellow incrustation; and by action on its solutions, of sulphuretted hydrogen or sulphide of ammonium to throw down a black precipitate insoluble in dilute acids, of sulphuric acid to throw down a white precipitate, of hydrochloric acid to throw down a white precipitate soluble in and crystallisable from boiling water, of iodide of potassium to throw down a yellow precipitate sparingly soluble in and crystallisable from boiling water, and of fixed caustic alkali to throw down a white precipitate soluble in excess of the precipitant.

(67.) Beryllium.

Beryllium, or glucinum, found native in form of silicate as phenakite $Be_2O_2.SiO_2$; in form of alumino-silicate as beryl or emerald $Be_3Al_2O_6.Si_6O_{12}$, and as euclase $Be_3Al_2O_6.Si_2O_4$; in form of aluminate as chrysoberyl $BeAl_2O_4$; and as a constituent of several other minerals. Association of beryllium with magnesium somewhat doubtful. Equivalent weight of beryllium 4·75. Its atomic weight, as a diad metal, 9·5, presumable only. Metal obtained by passing vaporised beryllium chloride over melted sodium. A white, highly malleable metal, of sp. gr. 2·1, and melting point below that of silver. Its permanency in the air, even

at a red heat. Its indifference to the action of even boiling water. Its solubility in dilute sulphuric and hydrochloric acids, with evolution of hydrogen.

Chloride, $BeCl_2$; made, in hydrated state, by dissolving beryllia in hydrochloric acid; and, in anhydrous state, by passing dry chlorine over ignited mixture of beryllia and charcoal. A fusible, volatile, deliquescent and very soluble salt.

Hydrate, BeH_2O_2 or $BeO.H_2O(?)$; thrown down, on addition of ammonia to beryllium chloride, as a white gelatinous precipitate, becoming pulverulent when dry. Its solubility in potash and soda, and reprecipitation on ebullition of the diluted liquids. Its solubility in cold aqueous ammonium carbonate as double carbonate of beryllium and ammonium, and its precipitation as simple carbonate on ebullition of the liquid. Its solubility also (with evolution of ammonia) in boiling solution of sal-ammoniac as double chloride of beryllium and ammonium. Its absorption, both in moist and dry state, of atmospheric carbonic acid. Its dehydration by ignition.

Oxide, BeO; made by igniting the hydrate or carbonate. A soft, bulky, white powder, of sp. gr. 2·97, tasteless and adherent to the tongue, rendered less soluble in acids but otherwise unaltered by strong ignition, and volatilised without fusion by heat of oxhydrogen blowpipe. Solubility of beryllium oxide, hydrate, and carbonate in most acids, to form crystallisable, colourless salts, having a characteristic sweetish taste.

Beryllia extracted from the native minerals by fusing them with quicklime or alkali carbonate, treating fused mass with excess of hydrochloric acid and evaporating down to separate silica, dissolving residue in dilute hydrochloric acid, and precipitating solution with ammonia. Beryllia then separated from alumina and ferric oxide by digesting the precipitate in cold ammonium carbonate, or by boiling it in ammonium chloride solution.

Resemblance of beryllium to aluminium in gelatinous character and solubility in fixed alkali of its precipitated hydrate, and in ready volatility of its chloride. Its difference from aluminium and resemblance to magnesium in the infusibility and pulverulent cha-

racter of its oxide; and in the solubility in carbonate of ammonium of, and decomposition of sal-ammoniac with evolution of ammonia, and absorption of carbonic acid by, its hydrate. Beryllium far less oxidisable than magnesium, and beryllia a feebler base than magnesia. Special tendency of beryllium to form basic salts.

Chrysoberyl $BeAl_2O_4$, heteromorphous with spinelle $MgAl_2O_4$.

(68.) Magnesium.

Magnesium found native to some extent as carbonate $MgCO_3$, in magnesite and calc-spar; but far more extensively, as a double calcium and magnesium carbonate, in magnesian limestone, dolomite, and bitter-spar. Abundant existence in nature of different silicates of magnesium, especially olivine $2MgO.SiO_2$, serpentine $Mg_3O_3.2SiO_2.2Aq$, picrosmine $H_2Mg_2O_3.2SiO_2$, hornblende and augite $MgO.SiO_2$, talc $H_2Mg_5O_6.6SiO_2$, steatite $Mg_3O_3.4SiO_2$, meerschaum $Mg_2O_2.3SiO_2.2\&4Aq$; and of alumino-silicates, more especially mica $Mg_4Al_2O_7\,4SiO_2$, and chlorite $MgAl_2O_4(Mg_3O_3.2SiO_2).3Aq$, the latter being the chief constituent of the different varieties of slate. Existence also of native magnesium hydrate MgH_2O_2, as brucite; hydrate-carbonate $MgH_2O_2.3(MgCO_3.H_2O)$, as hydro-magnesite; potassio-chloride $KCl.MgCl_2.6Aq$, as carnalite; aluminate $MgAl_2O_4$, as spinelle; borate MgB_2O_4, as boracite; sulphate $MgSO_4.6Aq$ (?), as bitter-salt; fluor-phosphate $Mg_2(PO_4)F$, as wagnerite; ammonio-phosphate $NH_4MgPO_4.6Aq$, as struvite; and of various other magnesium compounds. Occurrence of some dissolved acid-carbonate of magnesium in many natural waters, and of chloride and sulphate of magnesium to a large extent in sea-water and bitter mineral springs. Association of more or less magnesium with calcium in vegetable and animal kingdoms.

Commercial sources of magnesium-compounds; the carbonate, as magnesite and magnesian-limestone; the hydrated silicate, as serpentine; the sulphates, crystallised from mother liquors of sea-water, bitter-spring water, and produced from shale-alum works; and the chloride, extracted from sea-water and carnalite.

Magnesium obtainable by electrolysis of the fused chloride, mixed or not with chloride of alkali-metal; and in the moist way. Produced commercially by ignition together of sodium and chloride of magnesium, the latter mixed with some chloride of sodium and fluoride of calcium to facilitate fusion, &c. Reduced metal purified by distillation in a current of hydrogen.

Magnesium an almost silver-white metal, of sp. gr. 1·7, moderately malleable and ductile at ordinary temperatures, fusing at a red, and volatilising at a stronger heat. Its crystallisation in octahedrons (Becquerel). Its permanency in dry, and very gradual oxidation in moist air. Its combustion, with dazzling white flame, when heated to redness in air or oxygen. Its combustion also in chlorine gas and in bromine and iodine vapours.

Slow decomposition of water by magnesium, save on ebullition or after acidulation. Its rapid decomposition of most dilute acids, with evolution of hydrogen; and violent action on ordinary hydrochloric acid. Its combination with nitrogen to form the compound Mg_3N_2.

Chloride, $MgCl_2$; obtained in solution by deliquescence of natural or artificial carnalite, or by dissolving carbonate of magnesium, &c., in hydrochloric acid. Production, on evaporation, of prismatic very deliquescent hydrated crystals, $MgCl_2.6Aq$. Moist chloride of magnesium decomposed, to greater or less extent, by drying and igniting, into hydrochloric acid and magnesia:

$$MgCl_2 + H_2O = MgO + 2HCl$$

Combination of dissolved chloride of magnesium with chloride of alkali-metal to form hydrated crystalline compounds, as carnalite, $KCl.MgCl_2.6Aq$.

Anhydrous chloride of magnesium produced by evaporating down solution of mixed magnesium and ammonium chlorides, and igniting resulting double salt to expel sal-ammoniac; by evaporating down solution of magnesium chloride alone, in current of hydrochloric acid gas; or by passing chlorine gas over ignited mixture of magnesia and charcoal. A volatile,

readily fusible compound, solidifying into a crystalline deliquescent mass. Anhydrous double chloride of magnesium and sodium or potassium made by igniting the evaporated residue of a solution of the mixed chlorides.

Oxide, MgO. An insoluble, infusible, white solid, made by igniting the heavy or light artificial basic carbonate, or the nitrate, &c. Its gradual combination with water to form the hydrate, and alkaline reaction on wetted turmeric paper.

Hydrate, $Mg(HO)_2$ or $MgO.H_2O$; produced as above, and found native as brucite. Its precipitation from chloride of magnesium, &c., by means of lime-water. Its imperfect solubility, feeble alkalinity, and slow absorption of carbanhydride. Its easy dehydration by heat.

Sulphide and sulphydrate of magnesium insoluble, indefinite compounds.

Carbonate, $MgCO_3$; found native in amorphous masses as magnesite, or in rhombohedral crystals as talc-spar. Its production in hydrated prisms $MgCO_3.3Aq$, efflorescing on exposure into the prothydrate $MgCO_3.Aq$, by spontaneous evolution of the gas from a carbonic acid solution of magnesia alba, &c.

Basic carbonate, or hydrate-carbonate of magnesium, $Mg(HO)_2.3(MgCO_3.H_2O)$, found native as hydro-magnesite; made artificially as magnesia alba, by precipitating sulphate of magnesium with carbonate of sodium solution, at a boiling heat or with subsequent boiling:

$$4MgSO_4 + 4H_2O + 4Na_2CO_3 = MgO.H_2O.3(MgCO_3.H_2O) + 4Na_2SO_4 + CO_2$$

Composition of artificial product variable. Light variety obtained by washing and drying the precipitate formed from dilute solutions. Heavy variety obtained by evaporating down mixed stronger solutions and washing out sulphate of sodium from the evaporated residue. Solubility of different magnesium carbonates in carbonic acid water. Their conversion into magnesia at an incipient red heat.

Occurrence of double magnesium and calcium carbonate,

$MgCO_3.CaCO_3$ or $MgCa(CO_3)_2$, as rhombohedral crystals in bitter-spar, as crystalline rock in dolomite, and as amorphous rock in magnesian limestone. Frequent excess of calcium carbonate in last variety. Constituent magnesium carbonate of the compound decomposed at a moderate heat, leaving calcium carbonate unaffected. Extraction of magnesia from the product by carbonic acid water under pressure, and its deposition as carbonate on boiling the resultant solution.

Sulphate, $MgSO_4$; made by evaporating mother-liquor of sea-water or bitter spring water; by roasting pyritic serpentine, alum-shale, &c., digesting residue in water, and evaporating the solution, in latter case after separation of alum; and by dissolving in sulphuric acid the carbonate, hydrate, or hydrated silicate of magnesium, in forms of native magnesite, or as precipitate thrown down from crude magnesian chloride by lime-water, or as residue left after washing ignited magnesian limestone, &c. with water, or as native serpentine. Ordinary sulphate of magnesium, or Epsom salt, crystallised in small four-sided prisms with 7 atoms of water; soluble in 3 times their weight of cold, and $1\frac{1}{2}$ times their weight of boiling water (Miller). Hexahydrate found native, made by drying Epsom salt at 50–60°, or crystallising it from hot concentrated solution. Sulphate left dihydrated at 100° in vacuo, monohydrated at 130°, and anhydrous at 210° and upwards. Partial decomposition of anhydrous salt by strong ignition. Combination of sulphate of magnesium with sulphates of alkali-metals and ammonium to form crystalline salts, typical of large class of isomorphous compounds known as magnesian double sulphates. Their formation by substitution of alkali-sulphate for constitutional water (Graham), thus:

$MgSO_4.H_2O.6Aq$	Epsom salt
$MgSO_4.K_2SO_4.6Aq$	Double sulphate

Magnesium salts infusible before the blowpipe. Pinkish tint of residuary mass after its re-ignition with nitrate of cobalt. Sulphate, nitrate, chloride, acetate, &c., freely soluble, forming neutral solutions. Hydrate, carbonate, oxalate, phosphate, &c.,

insoluble in water, but soluble, except the phosphate, in presence of ammonia-salts. Magnesium recognised, after removal of terr-alkalis, by formation of crystalline precipitate of triple phosphate on adding alkali-phosphate to magnesian solution containing ammonia and ammonia-salt.

Magnesium differentiated from calcium by volatility of the metal and its anhydrous chloride; decomposibility by heat of its hydrated chloride; insolubility of its hydrate; solubility of its sulphate; and by its yielding double and for the most part soluble magnesium-ammonium compounds.

(69.) Zinc.

Abundant existence of native zinc in form of oxide ZnO, mixed with oxides of manganese and iron, in red zinc ore; as sulphide ZnS, in zinc-blende; as carbonate $ZnCO_3$, in calamine and zinc spar; and as hydrated silicate $2ZnO.SiO_2.Aq$, in prismatic calamine. Anhydrous zinc silicate $2ZnO.SiO_2$, found native as willemite; and other compounds also met with. Artificial zinc compounds procured from the metal.

Metallic zinc obtained chiefly from the native carbonate, sulphide, and oxide, the two former converted into the oxide by roasting. Original or produced oxide mixed with powdered anthracite, coke, coal, or charcoal, and mixture strongly heated in clay retorts of various construction. Zinc reduced, distilled off, and condensed in receivers. English process of *distillatio per descensum.* Crude metal fused and cast into ingots, &c., or sometimes purified by redistillation. Pure zinc obtained with difficulty by distillation, from porcelain retort, of mixed oxide or carbonate of zinc and charcoal, both in pure state. Partial purification of commercial metal by its fusion with deficit of nitre.

Zinc a hard, bluish-white, crystalline metal, of sp. gr. about 7·0, brittle at ordinary temperatures (?), malleable and ductile at 100° and upwards, brittle again and even pulverisable at 200°. Its melting point 412°, and boiling point 1100°. Superficial

oxidation of zinc, by exposure to moist air. Its brilliant combustion, with bluish-white flame, when strongly heated in air or oxygen. Its ready combination with the halogens at ordinary temperatures. Its solution in dilute acids with liberation of hydrogen, and in most metallic salts with reduction of heavy metal. Its solution also in warm aqueous potash and ammonia with liberation of hydrogen. Action promoted by presence of platinum or iron:

$$H_2O + KHO + Zn = H_2 + KHO.ZnO \text{ or } KHZnO_2$$

Use of zinc as the oxidisable metal in galvanic batteries; for coating iron, with formation of iron alloy; for alloying with copper to form brass and yellow metal; and for alloying with copper and nickel to form white metal, &c.

Chloride, $ZnCl_2$; producible by combination of the metal and halogen; usually made by dissolving zinc in aqueous hydrochloric acid. Carbonate of zinc added to the solution so as to precipitate any iron, after its peroxidation by chlorine water. Possibility of obtaining hydrated crystals, $ZnCl_2.2Aq$. Ordinary anhydrous compound obtained by evaporating down the solution. Act attended by some loss of hydrochloric acid, and formation of zinc-oxide or oxichloride. Chloride of zinc a white, very deliquescent, and soluble salt, fusing at 100°, volatilising slightly at boiling point of mercury, and distilling freely at a red heat. Its use as a bath in the laboratory; as a caustic in surgery; and, in solution, as an antiseptic. Its combination with zinc oxide or hydrate to form several oxichlorides; with ammonia, to form $ZnCl_2.4H_3N$, and other compounds; with alkali-metal- and ammonium-chlorides to form double salts—the strong solution of ammonium compound $2NH_4Cl.ZnCl_2$, being used in soldering operations.

Oxide, ZnO. Its occurrence, crystallised in six-sided prisms, in red zinc ore and furnace calamine. Artificial oxide made by burning the strongly heated metal in current of air, or, less commonly, by igniting the hydrate or carbonate, &c. Its unalterability by water, solubility in most acids to form zinc salts, acquisition

of temporary deep yellow colour by heat, and employment as a white pigment.

Hydrate, $Zn(HO)_2$ or $ZnO.H_2O$; producible in crystalline form; thrown down as a gelatinous precipitate from zinc solutions, preferably the nitrate, on addition of caustic alkali or ammonia. Its solubility in excess of both precipitants, and easy dehydration by heat.

Sulphide, ZnS. Its occurrence as zinc-blende, usually crystallised in rhombic dodecahedrons, semi-transparent, and of a dark or pale brown colour. Its conversion into sulphate or oxide by gentle or powerful roasting, and slow dissolution in sulphuric and hydrochloric acids. Hydrated sulphide of zinc thrown down as a white precipitate, by decomposing zinc salts with alkaline sulphydrate; passing sulphuretted hydrogen through alkaline or acetic zinc solutions; &c. Compound oxidisable on exposure to air, and readily soluble in dilute acids.

Carbonate, $ZnCO_3$; found native, crystalline or amorphous, as calamine. Its conversion into the oxide by gentle ignition. Precipitate formed on decomposing zinc solutions by alkali-carbonates, a basic or hydrate-carbonate of variable composition.

Sulphate, $ZnSO_4$; made commercially by roasting the native sulphide, &c.; or more commonly by dissolving the metal in dilute sulphuric acid, precipitating any iron (after its peroxidation by chlorine water) with zinc carbonate, and crystallising the solution. Ordinary zinc sulphate, or white vitriol, crystallised in four-sided prisms with seven atoms of water. Its isomorphism with, and general correspondence in behaviour to, sulphate of magnesium. Its formation of double sulphate, $ZnSO_4.K_2SO_4.6Aq$, &c., and of several basic salts.

Zinc compounds mostly infusible before the blowpipe. Temporary assumption of deep yellow colour by the heated residue. Its permanent green colour after re-ignition with nitrate of cobalt. Zinc recognised, in solution, by its precipitation as sulphide, either by sulphydrate of ammonium, or by sulphuretted hydrogen after addition of acetate of ammonium; its precipitation as basic car-

bonate by potassium or sodium carbonate; and its precipitation as hydrate by fixed caustic alkali or ammonia, and re-solution in excess of the precipitant.

(70.) Cadmium.

Cadmium found native as sulphide CdS, in greenockite. Its occurrence as an impurity in most zinc ores, and extraction from earliest portion of the metal or flowers produced in zinc smelting by solution in acid, and subsequent precipitation of cadmium from resultant solution, in metallic state by bars of zinc, or preferably as sulphide by sulphuretted hydrogen. Sulphide then dissolved in hydrochloric acid, solution precipitated by carbonate of ammonia, and the washed, dried, and ignited precipitate sublimed with charcoal.

A lustrous, bluish-tinted metal, whiter however than zinc, of sp. gr. 8·7, malleable, ductile, and sectile, somewhat harder than tin, crackling when bent, and becoming brittle and pulverisable at temperature of 82°. Its fusion at 115·5°, and crystallisation after fusion in octahedrons. Its volatilisation below boiling point of mercury, and ebullition at 860°. Specific gravity of its vapour 56 times that of hydrogen. Cadmium scarcely alterable at ordinary temperatures, even in moist air; but combustible at a red heat, with production of brown fumes. Its slow dissolution in hydrochloric and sulphuric, but ready solubility in nitric acid. Its combination with other metals to form highly fusible alloys, melting at 60° and upwards.

Chloride, $CdCl_2$; producible by dissolving the metal or oxide in hydrochloric acid. Its existence in form of hydrated crystals, $CdCl_2.2Aq$, and as a fused anhydrous mass. Its sublimation in micaceous crystals at a full red heat. Crystalline chloramide of cadmium $CdCl(NH_2)$, left by spontaneous evaporation of solution of cadmium chloride, mixed with excess of ammonia. Iodide of cadmium CdI_2, an anhydrous, crystalline, sparingly soluble, fusible salt, used in photography; made by digesting cadmium in iodine and water.

Oxide, CdO; a brown, amorphous or crystalline powder; usually made by burning the metal, or igniting the hydrate, carbonate, or nitrate. Its solubility in acids and aqueous ammonia. The hydrate $Cd(HO)_2$, formed by decomposing cadmium salts with fixed alkali-hydrate. White precipitate insoluble in excess of precipitant, soluble in ammonia.

Sulphide, CdS; found native as greenockite, in six-sided prisms. Hydrated sulphide formed, by passing sulphuretted hydrogen through cadmium solutions, as a bright yellow precipitate, soluble in not too dilute acids. Its use as a pigment.

Carbonate, $CdCO_3$(?); a white precipitate, thrown down on addition of alkali-carbonate to cadmium solutions.

Sulphate, $CdSO_4$; made by dissolving the metal or oxide in sulphuric acid. A white, somewhat efflorescent salt, crystallising usually with four atoms of water. Its solubility in water, and formation of double sulphate, $CdSO_4.K_2SO_4.6Aq$, &c.

Cadmium compounds decomposed before the blowpipe, with formation of dark brown pulverulent incrustation. Metal recognised in solution, by its precipitation by sulphuretted hydrogen as bright yellow cadmium sulphide, insoluble in sulphide of ammonium, insoluble in very dilute, but readily soluble in stronger, hydrochloric or sulphuric acid; also by its precipitation by fixed alkali or ammonia as cadmium hydrate, soluble in excess of ammonia; and by its precipitation by fixed alkali- or ammonia carbonate, as cadmium carbonate, insoluble in excess of either precipitant.

(71.) Mercury.

Mercury sometimes found native, disseminated through its principal ore, the sulphide HgS, or cinnabar. Its occurrence also, in forms of mercurous chloride, mercuric iodide, selenide, &c., and as silver amalgam.

Metal extracted by the process of roasting or combustion in peculiarly constructed furnaces, and resultant mercury condensed either in flues, or in a series of short clay cylinders called *aludels*,

fitting into one another so as to form continuous tubes, and lying on an inclined plane or aludel-bed:

$$HgS + O_2 = Hg + SO_2$$

Mercury sometimes obtained by distilling cinnabar with lime in iron retorts; and in other ways:

$$4HgS + 4CaO = Hg_4 + 3CaS + CaSO_4$$

Commercial mercury usually very pure. Purification of foul mercury by its exposure to air under oil of vitriol; or by its agitation with dilute nitric acid containing some nitrate of mercury in solution; or most efficiently by its redistillation, preferably in current of super-heated steam.

A freely mobile, highly conductive, metallic liquid, of sp. gr. 13·6, forming spherical globules. Its brilliancy and greyish-white colour. Its solidification at $-40°$, into a soft malleable metal, crystallising in regular octahedrons. Its ebullition at 350° into a colourless vapour, of sp. gr. 100. Its volatility at all temperatures above 10°, and to considerable degree in current of ordinary steam. Uniform dilatation of mercury by heat, to extent of $\frac{1}{55}$, between 0° and 100°.

Mercury reduced to the state of minute non-adherent globules by agitation with certain solutions, as of mercurous nitrate; and converted into non-lustrous powder or paste by being rubbed up with chalk, grease, &c. Its precipitation, in yet finer state of division, from solution of corrosive sublimate, for instance, by stannous chloride or other reducing agent.

Direct combination of mercury at ordinary temperatures with chlorine, bromine, and, especially on trituration, with iodine and sulphur. Its unoxidisability by mere exposure to air and moisture, but gradual absorption of oxygen at temperature of 300° or so, to form mercuric oxide. Its indifference even to boiling hydrochloric acid; but reaction with hydriodic and sulphydric acids to effect liberation of hydrogen. Its ready solubility in nitric acid to form either mercurous or mercuric nitrate, with reduction of a portion of the acid to the state of

nitric oxide. Its conversion, by sulphuric acid, at a gentle heat, into mercuric sulphate, with evolution of sulphurous anhydride.

Solution, real or apparent, of different metals in mercury. Separation of semi-solid amalgams, by forcibly filtering off the excess of mercury through leather, &c. Production of definite compounds as Ag_2Hg_2, CuHg, &c., by subjecting the crude amalgams to powerful pressure. Combination of mercury with basylous metals attended by a considerable extrication of heat.

Formation by mercury of two distinct series of compounds; namely, mercuric compounds, typified by corrosive sublimate or mercuric chloride $HgCl_2$; and mercurous compounds, typified by calomel or mercurous chloride HgCl or Hg_2Cl_2.

MERCURIC COMPOUNDS.

Chloride, $HgCl_2$; known as corrosive sublimate, producible by heating mercury with chlorine gas, and in other ways; usually made by subliming mixture of mercuric sulphate with common salt:

$$HgSO_4 + 2NaCl = HgCl_2 + Na_2SO_4$$

Transparent, white, crystalline masses, or prismatic crystals, of sp. gr. 5·42, fusing at 265°, and boiling at 295°. Sp. gr. of vapour $\frac{200+71}{2} = 135·5$. Mercuric chloride soluble in 16 parts of cold water, freely soluble in hot water, in alcohol, and in ether. Withdrawal of the salt from its aqueous solutions by their agitation with ether. Its free solubility also in aqueous solutions of alkali- &c. chlorides, including chloride of hydrogen, with formation of crystallisable double chlorides such as $KCl.HgCl_2.Aq$, &c. Corrosive sublimate solution characterised by its acrid, nauseous, metallic taste, acid reaction to test paper, coagulation of albumin, &c., whence its use as an antiseptic, and by its decomposition, with deposition of mercury, by copper and most metals, save silver, gold, and platinum. Its decomposition by other reducing agents, as stannous chloride, with precipitation

of calomel and finally of mercury,—by alkali- &c. hydrates and carbonates, with precipitation of mercuric oxide or oxichloride,—by sulphide of hydrogen, &c., with precipitation of the sulphide, or sulphochloride,—and by ammonia with precipitation of the chloramide or some allied compound. Indecomposibility of corrosive sublimate by sulphuric acid. The bromide $HgBr_2$, very similar to the chloride.

Iodide, HgI_2; made by triturating mercury with iodine; or, preferably, by mutual precipitation of mercuric chloride and iodide of potassium solutions. A bright scarlet, crystalline precipitate, soluble in excess of either reagent in form of a colourless double salt, $Hg_3Cl_4I_2$ or $KHgI_3$; and also in various alkali-chlorides, iodides, and ammonium salts. Insolubility of mercuric iodide in water; its solubility in alcohol especially at a boiling heat, and to a less degree in ether. Solubility of excess of mercuric iodide in boiling iodide of potassium solution, and its deposition on cooling in scarlet octahedrons belonging to the square prismatic system. Specific gravity of mercuric iodide 6·2. Its assumption of a bright yellow colour when heated. Its fusion and volatilisation at about 200°, and deposition on cooling in yellow rhombic tables or prisms. Consequent dimorphism of the red and yellow varieties. Conversion of the yellow into the red variety, gradual when spontaneous, but immediate as a result of friction. Occasional precipitation of the yellow (soon, however, changing into the red) variety on adding iodide of potassium to mercuric chloride, on diluting the alcoholic solution of mercuric iodide with water, &c.

Oxide, HgO. Existence of red or crystalloid, and yellow or amorphous varieties of the oxide. Red variety made, in form of scales, by heating mercury to near its boiling point, with exposure to air for some days; or in crystalline grains, by heating any nitrate of mercury somewhat strongly until quite decomposed. Red oxide rendered temporarily black by heat.

Yellow oxide made by adding solution of corrosive sublimate to excess of dissolved caustic alkali or alkaline earth. Precipitate at first hydrated, but rendered anhydrous by desiccation.

Greater susceptibility of yellow than of red oxide to chemical agents as chlorine, corrosive sublimate, oxalic acid, &c., probably due to a difference of physical condition (?).

Both varieties readily soluble in most acids to form mercuric salts; just soluble in water to form perceptibly alkaline liquid; decomposible at red heat into oxygen and mercury; and occasionally used as oxidising agents. Indifference of mercuric oxide to carbonic acid or anhydride. Non-existence of a definite mercuric carbonate.

Existence of several oxichlorides of mercury, producible by action of chlorine on mercuric oxide, combination of mercuric chloride with the oxide, imperfect decomposition of the chloride by alkali-hydrocarbonate, or by deficit of neutral carbonate or hydrate, &c. &c. Best defined compound $Hg_3Cl_2O_2$ or $HgCl_2.2HgO$, obtained in dense black crystalline state, by action of dissolved chlorine on precipitated oxide of mercury, or by addition of one volume of saturated solution of acid carbonate of potassium to two of corrosive sublimate solution. With larger and larger volumes of sublimate solution, the same compound obtained as a violet red crystalline, or brick red amorphous precipitate.

Sulphide, or cinnabar, HgS. Its occurrence in massive, fibrous, or crystalline state, as the chief ore of mercury. Artificial compound, or vermillion, made by finely levigating the sublimate furnished by an intimate mixture of sulphur and mercury. Vermillion also made in the wet way by thoroughly commixing mercury, sulphur, and concentrated solution of pentasulphide of potassium, allowing the action to go on for some days at a gentle heat, and finally washing the product with caustic soda to remove excess of sulphur. Sulphide of mercury ordinarily procured as a dense black precipitate by acting on mercuric salts with excess of sulphide of hydrogen or of alkali-metal, &c. Its conversion into the red compound by sublimation.

Crystallisation of mercuric sulphide in hexagonal prisms. Its sublimation without prior fusion. Correspondence of volatilised sulphide to three volumes of vapour, owing to its dissociation

into Hg (2 vols.), and S (1 vol.)? Liberation of mercury from cinnabar by roasting it in air, heating it with iron or lime, &c. Its resistance to action of hydrochloric or nitric acid, but gradual solution in aqua-regia.

Existence of mercuric sulphochloride $Hg_3Cl_2S_2$, formed as a yellowish precipitate by treating solution of mercuric chloride with deficit of sulphuretted hydrogen.

Amides, &c. Ammoniated mercuric chloride, $NH_3.HgCl_2$ or $Hg\underbrace{NH_2}Cl.HCl$, made by heating corrosive sublimate in a current of dry ammonia. A white, fusible, volatilisable compound, decomposible by water.

White precipitate, or mercuric chloramide $Hg\underbrace{NH_2}Cl$, made by adding corrosive sublimate solution to excess of aqueous ammonia:

$$HgCl_2 \quad + \quad 2NH_3 \quad = \quad Hg\underbrace{NH_2}Cl \quad + \quad NH_4Cl$$

A white powder, turned yellow by potash with evolution of ammonia, soluble in nitric or hydrochloric acid, and decomposible by heat. Fusible white precipitate, $N_2H_6.HgCl_2$ or $Hg\underbrace{NH_2}Cl.NH_4Cl$, made by boiling above white precipitate in solution of sal-ammoniac; or by adding corrosive sublimate to hot solution of sal-ammoniac and ammonia until the resulting precipitate ceases to be redissolved. Compound deposited on cooling in octahedral crystals. Also thrown down at once as a white amorphous precipitate by adding caustic or carbonated alkali to solution of corrosive sublimate in sal-ammoniac. Its fusion, with decomposition, by heat.

Hydrochloride of dimercuro-chloramine $Hg_2\underbrace{NH''}Cl_2.HCl$, a white precipitate thrown down by gradual addition of ammonia to excess of corrosive sublimate solution.

Hydrochloride of dimercuroxamine $Hg_2\underbrace{NH''}O.HCl$, a canary yellow powder made by boiling either form of white precipitate with excess of water, or saturating hydrate of dimercuroxamine with hydrochloric acid:

$$2Hg.\underbrace{NH_2}Cl \quad + \quad H_2O \quad = \quad Hg_2\underbrace{NH}O.HCl \quad + \quad NH_4Cl$$

Hydriodide of dimercuroxamine, $Hg_2NHO.HI$, a brown precipitate formed by action of ammonia on potash solution of double iodide of mercury and potassium.

Dimercuroxamine hydrates* $Hg_2NHO.H_2O$ & $Hg_2NHO.2H_2O$, producible in various ways; best made by agitating precipitated mercuric oxide with ammonia in a closed bottle, and drying resultant yellowish-white powder, in the dark over quicklime to form the dihydrated compound, or in vacuo over oil of vitriol to form the monohydrate. An unstable, explosive, powerfully basic substance, decomposing ammoniacal salts with evolution of ammonia; neutralising acids to form salts, as the hydrochloride $Hg_2NHO.HCl$, the sulphate $(Hg_2NHO)_2H_2SO_4$, &c.; and absorbing atmospheric carbonic acid to form the carbonate $(Hg_2NHO)_2H_2CO_3$.

Nitride, Hg_3N_2; made by passing dry and cold ammonia gas over dried yellow oxide of mercury. A dark brown explosive powder, dissolving in acids to form mercuric and ammonium salts.

Nitrates. Salts producible by solution of mercury in excess of nitric acid, but best made by saturating nitric acid with mercuric oxide. Hydrated normal nitrate $2Hg(NO_3)_2.H_2O$, obtained in large crystals by evaporating solution of mercuric oxide in excess of strong nitric acid. Hydrated nitrate-hydrate $2Hg(NO_3)HO.H_2O$, the ordinary variety of mercuric nitrate, made by saturating dilute nitric acid with mercuric oxide, or by dissolving metallic mercury in an excess of the acid. Its crystallisation in small needles. Mercurated nitrate-hydrate $2Hg(NO_3)HO.HgO$, a yellow insoluble salt, precipitated on freely diluting the solution of either of the above nitrates. Its eventual transformation into mercuric oxide by prolonged washing with boiling water.

* $ClHg(NH_2)'.HCl$	Hydrochloride of	mercuric chloramide.	
$Cl_2Hg_2(NH)''.HCl$	„	„ dimercuro-chloramide.	
$OHg_2(NH)''.HCl$	„	„ dimercuroxamine.	
$OHg_2(NH)''.H_2O$	Hydrate	„	„

Sulphate, $HgSO_4$; made by heating mercury with oil of vitriol:

$$2H_2SO_4 + Hg = HgSO_4 + 2H_2O + SO_2$$

A white crystalline powder, becoming temporarily darker by heat, and undergoing partial decomposition and partial sublimation at a stronger heat. Its immediate decomposition by water, with formation of a yellow basic salt known as turpeth mineral. Solution of some mercuric sulphate in the liberated acid, as an acid salt:

$$3HgSO_4 + 2H_2O = HgSO_4.2HgO + 2H_2SO_4$$

Reaction of mercuric sulphate with chloride of hydrogen, chloride of sodium, &c., to form corrosive sublimate:

$$HgSO_4 + 2HCl = HgCl_2 + H_2SO_4$$

MERCUROUS COMPOUNDS.

Their representation as the analogues of silver salts with substitution of Hg′ for Ag′; or as the analogues of mercuric salts with substitution of Hg_2 or Hhg″ for Hg. Alleged semi-saturation of mercury by mercury in mercurous salts?

$$ClH''gCl + H''g = ClH''gH''gCl$$

Chloride, or calomel, HgCl or $HhgCl_2$; producible by precipitation of mercurous salts with chloride of sodium, &c., and of corrosive sublimate solution by reducing agents; but usually made by subliming a mixture of corrosive sublimate and mercury, or a mixture of mercuric sulphate and mercury with common salt:

$$HgSO_4 + Hg + 2NaCl = Na_2SO_4 + HhgCl_2$$

Vapour condensed as a soft white powder in large chambers charged with steam; or as a semi-transparent crystalline cake, afterwards ground with water to the state of white or brownish-white powder. Volatility of calomel without fusion, below a red heat, and its condensation in four-sided prisms. Vapour density $\frac{200+35.5}{2} = 117.75$. Partial decomposition (dissociation?) of

calomel during sublimation, whence necessity for washing the product to remove any corrosive sublimate.

Decomposition of calomel by dissolved fixed alkalis, with production of mercurous oxide, as in black wash:

$$HhgCl_2 + Ca(HO)_2 = CaCl_2 + HhgO + H_2O$$

Its decomposition by aqueous ammonia, with formation of black mercurous chloramide:

$$HhgCl_2 + 2NH_3 = Hhg(NH_2)Cl + NH_4Cl$$

Its direct absorption of ammonia gas to form black mercurous diammonium chloride, $N_2H_6Hh''gCl_2$ or $HhgNH_2Cl.NH_4Cl$, breaking up into ammonia and calomel on exposure to air.

Indifference of calomel to sulphuric acid; its solubility both in chlorine water and strong nitric acid, in form of corrosive sublimate, &c.; and its partial decomposition into mercury and corrosive sublimate by exposure to sunlight, or ebullition with chlorides of hydrogen, ammonium, sodium, &c. Mercurous bromide very similar to the chloride.

Iodide, HgI or $HhgI_2$; made by triturating mercury with iodine, or by precipitating dissolved mercurous salts with iodide of potassium. Greenish yellow, very unstable powder, susceptible however of sublimation.

Oxide, Hg_2O or HhgO. An unstable black powder, made by levigating calomel with excess of dissolved alkali. Washed product then dried spontaneously in absence of light. Its ready decomposition into mercury and mercuric oxide, and non-volatilisability. Its saturation of acids to form mercurous salts.

Sulphide, Hg_2S or HhgS; a similar unstable black compound, formed by levigating mercury with sulphur (ethiops mineral), or decomposing mercurous salts with sulphuretted hydrogen, &c.

Nitrates. Normal salt (*a*) $Hhg(NO_3)_2.2Aq$, produced in rhombic tables, or six-sided prisms (Gerhardt), by digesting mercury for some time with cold dilute nitric acid. Its solubility in dilute nitric acid, and in small quantity of cold water. Basic

salt (*b*) $Hhg(NO_3)HO$, produced as a yellow precipitate by decomposing the normal and intermediate nitrates with excess of warm water. Apparent existence of three intermediate salts:

a	+	*b*	$Hhg_2(NO_3)_3HO$	(Marignac)
a	+	2*b*	$Hhg_3(NO_3)_4(HO)_2$	(Gerhardt)
a	+	4*b*	$Hhg_5(NO_3)_6(HO)_4$	(Marignac)

Different intermediate salts made by digesting mercury in the solution of, or in mother-liquor from, the normal salt. The first two soluble in small quantity of water, and sometimes mistaken for the normal salt. Distinguished from it, by yielding, instead of calomel, a grey mixture of calomel and mercurous oxide, when rubbed up with moist common salt. Composition of the black precipitate formed by action of ammonia on dissolved mercurous nitrate, variable, most usually $Hhg_3(NO_3)_2(NH_2)_2(HO)_2$.

Carbonate, Hg_2CO_3 or $HhgCO_3$; an unstable yellowish white precipitate, produced at first in form of the hydrate $HhgCO_3.H_2O$, by decomposing solution of mercurous nitrate with excess of alkali-carbonate.

Sulphate, Hg_2SO_4 or $HhgSO_4$; produced in manufacture of mercuric sulphate; made by levigating mercuric sulphate with mercury. Salt obtained by deposition from oil of vitriol in minute crystals, not decomposible by washing with water.

Mercury compounds characterised by their volatility, and by their yielding a sublimate of mercurial globules when heated with carbonate of sodium. Mercury salts in solution recognised by their giving with sulphuretted hydrogen a black precipitate of sulphide, insoluble even in nitric acid; by their giving with stannous chloride a white precipitate of calomel and a grey precipitate of reduced mercury in succession; and by their depositing on copper foil a mercurial coating procurable as a sublimate upon the application of heat.

Mercuric distinguished from mercurous salts by their non-precipitability by chloride of hydrogen and chlorides generally; and by their giving with fixed caustic alkalis a bright yellow

precipitate of mercuric oxide, and with iodide of potassium a bright scarlet precipitate of mercuric iodide.

Mercurous distinguished from mercuric salts by their giving with hydrochloric acid and chlorides generally a white precipitate of calomel, with caustic alkalis a black precipitate of mercurous oxide, and with iodide of potassium a greenish-yellow precipitate of mercurous iodide.

CHAPTER VIII.

(72.) ALUMINIUM—TIN ELEMENTS.

EARTH-METALS proper characterised by the insolubility of their oxides and hydrates, the inseparability of their anhydrous chlorides from aqueous solution, and the non-producibility of their sulphides in the moist way. Diad earths typified by magnesia, triad by alumina, tetrad by zirconia, and pentad by tantalia. Association of zirconium with less basylous metal titanium, and, through titanium, with reguline and easily sulphurettable metal tin. Consideration in this chapter of triad metal aluminium, and tetrad metals tin, titanium, and zirconium.

Triad.			Tetrad.		
Al	Aluminium	27·5	Si	Silicon	28
			Sn	Tin	118
			Ti	Titanium	50
			Zr	Zirconium	89·5

Aluminium a malleable conductive metal, replacing the hydrogen of hydrochloric acid in the ratio of one atom of metal to three atoms of hydrogen, or of two atoms of metal to six atoms of hydrogen, to form a fusible volatile chloride, having the formula Cl_3Al, or $Cl_6All = Cl_6Al_2$. Probable association of metallic aluminium with non-metallic boron, illustrated by analogy of spinelle $MgAl_2O_4$, to boracite MgB_2O_4; of aluminic ethide Et_3Al to boric ethide Et_3B, &c. Preconsidered metals thallium and gold also characterised by the property of forming triad compounds, as thallic chloride Cl_3Tl, auric chloride Cl_3Au, &c.

Formation by silicon, tin, titanium, and zirconium of mutually

analogous, well-defined, volatile tetrachlorides, tetrafluorides, &c., instanced by stannic chloride Cl_4Sn, and of corresponding isomorphous insoluble dioxides or anhydrides. Formation also, especially by tin, of a series of diad compounds exemplified by stannous chloride Cl_2Sn. Relationships of stannous to stannic and of plumbous to plumbic compounds parallel with one another.

Brief notices also included in this chapter of rare earth-metals thorium, yttrium, erbium, cerium, lanthanum and didymium, and of newly discovered reguline metal indium.

(73.) Aluminium.

Aluminium by far the most abundant of the metallic elements, and as a terrestrial constituent inferior only in quantity to oxygen and silicon. Its non-participation in processes of animal and vegetable life. Its occurrence in great variety of well-defined minerals; and in complex rocks, slates, shales, clays, &c. Principal aluminous minerals, the oxide Al_2O_3, or alumina, found native as corundum, emery, sapphire, and ruby. The double oxides, diaspore $H_2Al_2O_4$, chrysoberyl $BeAl_2O_4$, spinelle $MgAl_2O_4$, gahnite $ZnAl_2O_4$, &c.; and the double fluoride, cryolite Na_3AlF_6. Existence of several simple silicates, and especially of kaolin or pure clay $Al_2O_3.Si_2O_4.2Aq$. Topaz an anhydrous silicate of aluminium $Al_2O_3.SiO_2$, with some oxygen replaced by fluorine. Almost infinite number of double aluminous silicates, more especially felspar $K_2Al_2O_4.Si_6O_{12}$, the chief constituent of granite, gneiss, syenite, porphyry, basalt, greenstone, trachyte, obsidian, and pumice; common mica $Mg_4Al_2O_7.Si_4O_8$, also an important constituent of granite, gneiss, &c.; and chlorite $MgAl_2O_4.(Mg_3O_3.Si_2O_4).3Aq$, occurring both as a distinct mineral, either crystalline or massive, and as the basis of different varieties of slate. Other important or interesting double alumino-silicates exemplified by albite $Na_2Al_2O_4.Si_6O_{12}$; potash mica $K_2Al_6O_{10}.Si_6O_{12}$; labradore $CaAl_2O_4.Si_3O_6$; garnet $Ca_3Al_2O_6.Si_3O_6$; emerald or beryl $Be_3Al_2O_6.Si_6O_{12}$; and by numerous hydrated alumino-silicates principally of calcium known as zeolites, such for instance

as stilbite $CaAl_2O_4.Si_6O_{12}.6Aq$, prehnite $Ca_2Al_2O_5.Si_3O_6.Aq$, &c. Existence also of tourmaline or schorl, represented approximatively by formula $Mg_3Al_{12}B_4O_{27}.Si_9O_{18}$ or $(M''M''')O_3.SiO_2$; and of a peculiar sulphuretted sodio-aluminic silicate known as lapis-lazuli.

Aluminium first obtained by acting on aluminic chloride with potassium (Wöhler). Afterwards by electrolysis of fused sodio-aluminic chloride (Bunsen). Its producibility also by electrolysing cyanide of potassium solution of alumina, by igniting sodio-aluminic fluoride (cryolite) in current of hydrogen, &c. Metal now produced on manufacturing scale by reduction of sodio-aluminic chloride or fluoride with sodium. In most successful process, 10 parts of finely pulverised mixture of sodio-aluminic chloride and 5 parts of fluor-spar to promote fusion (or preferably cryolite) mixed with 2 parts of sodium in small ingots, and thrown on to hearth of previously heated reverberatory furnace. Reaction soon set up with great extrication of heat. Resulting fused metal and slag then run out from back of furnace:

$$2NaAlCl_4 \quad + \quad 3Na_2 \quad = \quad 8NaCl \quad + \quad Al_2$$

Aluminium a brilliant bluish white metal, of sp. gr. 2·56, increased by hammering. Its malleability, ductility, and tenacity very considerable. Its hardness about equal to that of silver, but increased to a marked extent by hammering. Metal characterised by a fair degree of elasticity, and a very striking sonority. Its fusion at a little below the melting power of silver, without suffering oxidation, and its ready capability of being granulated, cast into moulds, &c. Its crystallisability by way of fusion in octahedral forms. Its non-volatilisability. Its excellent conductivity, great specific heat, and slight paramagnetism.

Non-oxidation of aluminium, even when strongly heated in current of air. Its combustibility however in oxygen gas, and violent combination with chlorine and bromine. Its capability of being heated to redness in sulphur vapour without change; but combination therewith at a yet higher temperature. Aluminium unacted upon by pure water, hot or cold; and but slightly

affected by ignition in a current of steam. Its greater or less corrosion, however, by ebullition with acidulous, alkaline, and even saline water. Its indifference to sulphydric acid and alkaline sulphides. Its indifference also, at ordinary temperatures, to nitric acid, strong or dilute, and but slight attackability thereby even at boiling heat. Its ready solubility in hydrochloric acid, strong or dilute; and also in moderately strong sulphuric acid. Rapid dissolution of aluminium in heated solutions of caustic alkali, with evolution of hydrogen:

$$6KHO + Al_2 = 2K_3AlO_3 + 3H_2$$

Frosting of aluminium by immersing the metal in solution of caustic alkali, then washing it with water, and digesting it in nitric acid.

Chief uses of aluminium, for ornamental purposes; on account of its lightness, for the mechanical parts of astronomical, optical, and other philosophical instruments; as a speculum metal; and for alloying, more especially with silver and copper. Aluminium-bronze, composed of 90 parts copper and 10 parts aluminium, a beautiful gold-coloured alloy, susceptible of high polish, very hard, malleable, and tenacious.

Fluoride, $AllF_6$, or AlF_3; a crystallisable compound, little known in the isolated state; but producible artificially, and found native, in combination with fluoride of sodium, as cryolite Na_3AlF_6 or $3NaF.AlF_3$. A colourless, transparent, readily fusible mineral, occurring in crystalline and massive states. Its opacity after fusion. Its decomposibility by oil of vitriol, with evolution of hydrofluoric acid; and, at a red heat, by sodium, with separation of aluminium.

Chloride, $AllCl_6$, or $AlCl_3$; producible in solution by saturating hydrochloric acid with precipitated alumina, and in hydrated deliquescent crystals $AlCl_3.6Aq$, by evaporation of solution. Decomposition of salt by desiccation into alumina and hydrochloric acid:

$$2AlCl_3 + 3H_2O = Al_2O_3 + 6HCl$$

Anhydrous aluminium chloride formed by passing dry chlorine gas over intimate mixture of alumina and charcoal at a full red heat, and condensed as a yellowish semi-crystalline sublimate:

$$Al_2O_3 \quad + \quad C_3 \quad + \quad Cl_6 \quad = \quad 2AlCl_3 \quad + \quad 3CO$$

A difficultly fusible, readily volatilisable solid. Its vapour-density $\frac{55+213}{2} = 134$, corresponding to molecule $AlIlCl_6$. Its violent combination with water. Its evolution of hydrochloric acid and deliquescence in moist air; its solubility in absolute alcohol. Sodio-chloride of aluminium $NaCl.AlCl_3$ or $NaAlCl_4$, made by passing chlorine gas over ignited mixture of alumina, charcoal, and common salt. A white, readily fusible, deliquescent solid, volatile at a strong red heat.

Bromide, $AlIlBr_6$ or $AlBr_3$. Violent combination of aluminium with gently heated bromine to form the anhydrous compound, as a white, crystalline, fusible, volatile solid. The iodide $AlIlI_6$ or AlI_3, a very similar compound, made by heating aluminium with iodine in sealed tubes. Both salts formed in solution by dissolving the metal in hydrobromic and hydriodic acids respectively, and obtainable on evaporation in hexa-hydrated crystals.

Oxide or alumina, $AlIlO_3$ or Al_2O_3; found native as sapphire or ruby, and corundum; also, in impure state as emery. Occurrence of corundum, &c. in six-sided prisms, inferior only to the diamond in hardness, and of sp. gr. 3·95. Artificial alumina made by igniting the hydrate or nitrate; or by strongly igniting the sulphate or ammonio-sulphate. Complete decomposition of the sulphates difficult, facilitated by addition of ammonia from time to time. Artificial alumina a white porous solid, rendered compact and hard by prolonged heating. Its acquisition of a bright blue colour by ignition with nitrate of cobalt solution. Fusibility of alumina before the oxihydrogen blowpipe into a viscid liquid, solidifying into a transparent glass. Resistance of crystallised or compact alumina to action of sulphuric and other acids. Its reaction, however, with acid sulphate

of potassium, alkali-hydrate or carbonate, lime, silica, &c., under more or less powerful ignition:

$$K_2CO_3 + Al_2O_3 = K_2Al_2O_4 + CO_2$$
$$CaO + 2SiO_2 + Al_2O_3 = CaAl_2O_4.Si_2O_4$$

Hydrate, $All(HO)_6$ or $Al(HO)_3$; usually made by decomposing dilute solutions of nitrate, chloride, or sulphate of aluminium with excess of ammonia. Difficulty of removing last traces of basic salt from precipitate yielded by the sulphate or double sulphate. Resulting transparent, white, gelatinous precipitate thoroughly washed, and dried at 100°. Product obtained as a tough translucent, or opaque friable, hygroscopic mass, adhering to the tongue. Its dehydration upon gentle ignition, with sudden incandescence and great contraction of volume:

$$2Al(HO)_3 \text{ or } 2H_3AlO_3 = Al_2O_3 + 3H_2O$$

Occasional substitution of fixed alkali carbonate, or else of sulphydrate or carbonate of ammonia, &c., for caustic ammonia, as a precipitant of alumina. Gelatinous hydrate of aluminium also thrown down from aluminate of sodium solution, by addition of chloride, &c. of hydrogen or aluminium:

$$Na_3AlO_3 + AlCl_3 + 3H_2O = 3NaCl + 2H_3AlO_3$$

Saturation of acids by gelatinous alumina to form aluminium salts, with liberation of water. Its non-combination, however, with the carbonic and sulphydric acids. Aluminium salts for the most part soluble in water, to form solutions having a sweetish astringent taste and acid reaction. Solubility of aluminium hydrate in normal salts, to form different basic salts. Its solubility also in fixed caustic alkali, to form aluminates decomposible by addition of sal-ammoniac with precipitation of hydrated alumina:

$$K_3AlO_3 + 3NH_4Cl = 3NH_3 + H_3AlO_3 + 3KCl$$

Deposition of aluminium hydrate, $Al(HO)_3$ or H_3AlO_3, in small transparent regular crystals, and in semi-crystalline grains,

&c., from solution of aluminate of alkali-metal exposed to carbonic acid of the air.

Aqueous solution of aluminium hydrate procurable by dialysing its solution in chloride or acetate of aluminium. A viscid liquid of very feebly alkaline reaction, capable of being used for mordanting, and having a strong tendency to gelatinise, either spontaneously or upon addition of very minute quantity of almost any acid or salt. Jelly readily soluble in excess of acid. Aqueous solution of another hydrate of aluminium (metalumina) incapable of acting as a mordant, made by keeping the ordinary di-acetate solution at a boiling heat in close vessels for some days, until decomposed into metalumina and free acetic acid; the latter got rid of by ebullition or dialysis. This solution also gelatinised by addition of various acids and salts. Resulting jelly, however, insoluble in dilute acids. Composition of residue left on drying the solution at 100°, $2H_2O.Al_2O_3$. Occurrence of the hydrate $H_2O.Al_2O_3$ or $H_2Al_2O_4$, as a well-defined, translucent, semi-crystalline mineral known as diaspore. Its decrepitation on ignition, and insolubility in hydrochloric acid even when boiling. Bauxite another native hydrate, opaque, amorphous, and containing a considerable proportion of ferric oxide or hydrate.

Aluminates. That of sodium Na_3AlO_3, or $Na_6Al_2O_6$, produced on commercial scale by igniting bauxite with sodium carbonate, lixiviating product and evaporating down solution. A white amorphous solid, infusible by heat of reverberatory furnace, scarcely deliquescent, freely soluble in water. Spontaneous decomposition of the concentrated solution, with precipitation of coherent deposit, $Na_2Al_2O_4$ (?). Stability of more dilute solution out of access of air. Precipitation from it of gelatinous alumina by carbonic, hydrochloric, &c. acids, by salts of aluminium, as the chloride, &c., and by sal-ammoniac.

Potassium aluminate $K_2Al_2O_4$, produced by ignition of alumina with potassium carbonate; and, as a granular deposit, by evaporating down potash solution of alumina out of contact with air (Frémy). Analogous aluminates found native as chrysoberyl $BeAl_2O_4$, spinelle $MgAl_2O_4$, gahnite $ZnAl_2O_4$, &c.

Sulphates. The hydrated normal salt $Al_2(SO_4)_3.18Aq$, found native as feather alum or hair-salt. Also produced artificially by gently igniting pure clay, grinding burnt mass to powder, and heating the powder with sulphuric acid of sp. gr. 1·45 (*i.e.* chamber acid) in a reverberatory furnace. Product exposed to air for some days and extracted with water. Resulting solution freed from iron, by cautious addition of prussiate of potash, and evaporated down, so as to solidify upon cooling into a crystalline mass, known in commerce as concentrated alum. The salt obtainable, with difficulty, crystallised in thin pearly laminæ, very soluble in water, insoluble in alcohol. The anhydrous sulphate produced as a white porous mass by gently heating the hydrate. Also as a white powder by cooling a solution of the salt in oil of vitriol. Its insolubility in water, save after its gradual conversion into the hydrate. A basic sulphate $Al_2\left\{\begin{matrix}O_2\\SO_4\end{matrix}\right..3Aq$, found native as aluminite in form of white opaque mass. Same compound precipitated by adding deficit of ammonia to solution of the normal sulphate.

Double sulphates. Characteristic combination of aluminic sulphate with alkali sulphates, more especially of potassium and ammonium, to form the double salts or alums, $KAl(SO_4)_2.12Aq$ and $NH_4Al(SO_4)_2.12Aq$, crystallising in regular system, and usually in octahedrons. Salts made by direct addition of sulphate of potassium or ammonium to sulphate of aluminium. In practice, crude sulphate of aluminium made in solution by heating burnt clay or clay-slate with diluted sulphuric acid, and excess of acid neutralised with crude carbonate of ammonium (distilled gas-liquor) to form sulphate of ammonium. Or crude aluminic sulphate obtained more commonly by the roasting or weathering of pyritic shales; and resulting sulphates of aluminium, magnesium, and iron extracted with water. Solution then mixed with sulphate of ammonium, or with sulphate or chloride of potassium, the chloride being preferable from its conversion of any ferrous sulphate into the more soluble ferrous chloride. Mixture of the concentrated solutions sometimes made in the cold so as to precipitate alum-meal, afterwards washed and crystallised. More

often, the alkali-salt added to hot aluminic solution, and resulting alum crystallised out upon cooling and purified by recrystallisation. Alum also made, at Tolfa near Rome, by gently calcining native alumstone and extracting product with water:

$$KAl(SO_4)_2.Al_2H_6O_6 = KAl(SO_4)_2 + Al_2O_3 + 3H_2O$$

Product quite free from any soluble iron compound, but discoloured with ferric oxide, and known as roche or Roman alum.

Alum very soluble in boiling water, and sparingly soluble in cold water to form a sweetish-tasting astringent solution of marked acid reaction. Ready crystallisation of alum, upon cooling of hot concentrated solution, or by spontaneous evaporation, in simple or variously modified octahedrons. Its production in cubes when crystallised in presence of the basic salt, at temperatures not exceeding 50°. Roman alum usually crystallised in cubes. Fusion of alum in its water of crystallisation. Further action of heat upon potash alum to leave an infusible, porous, difficultly soluble mass of anhydrous or burnt alum, and eventually to expel a considerable proportion of sulphuric anhydride from the alumina. Action of a strong heat on ammonia alum to leave a residue of alumina, contaminated however with some basic sulphate. Partial decomposition of alum in solution by diffusion of alkali-sulphate away from sulphate of aluminium.

Formula for alum $M'M'''(SO_4)_2.12Aq$ or $M'_2M'''_2(SO_4)_4.24Aq$. Monad metal represented not only by potassium and ammonium, but also by sodium, rubidium, cæsium, thallium, silver, ethyl-ammonium, &c. The sodium salt not producible commercially, on account of its solubility. Silver alum completely decomposed by water. Triad metal represented not only by aluminium, but also by chromicum, ferricum, manganicum, &c. The chrome alums very stable and readily crystallisable compounds, of a fine violet colour. Existence also of a class of pseudo-alums, represented by native manganous aluminium sulphate $Mn''Al_2(SO_4)_4.22Aq$. These salts characterised by containing a diad instead of a monad metal, by their having a fibrous

instead of an octahedral form, and by their retaining a different proportion of crystallisation water.

Phosphates. Composition of the mineral gibbsite, formerly thought to be a hydrate of aluminium, expressed approximatively by formula $Al(PO_4).2Aq$ or $Al_2(PO_4)_2.4Aq$. Another hydrated normal phosphate, $Al(PO_4).3Aq$ or $Al_2(PO_4)_2.6Aq$, thrown down as a gelatinous precipitate upon addition of aluminic chloride to excess of sodium phosphate solution. The precipitate, dissolved in acid and again thrown down by ammonia, said to have the composition $Al_8\left\{\begin{matrix}O_3\\(PO_4)_6\end{matrix}\right..18Aq$. Expression by this formula, or by $Al_6\left\{\begin{matrix}O_3\\(PO_4)_4\end{matrix}\right..12Aq$. of mineral wavellite, with however some replacement of oxygen by fluorine. Existence of various complex native phosphates of aluminium.

Silicates. Principal silicates of aluminium already referred to. The anhydrous crystalline compounds undecomposible by acids, save the hydrofluoric. An important class of hydrated crystalline aluminous silicates known as zeolites, characterised by boiling up before the blowpipe, and undergoing complete decomposition by acids with separation of gelatinous silica. Clay-slate readily attacked by sulphuric acid, especially after gentle ignition. Pure clay $Al_2O_3.Si_2O_4.2Aq$, a product of the weathering of felspathic rocks. Its frequent admixture with rock detritus, silica, lime, magnesia, potash, and ferrous oxide. Pure clay insoluble in water, miscible therewith in any proportion and separable from excess of water by slow subsidence. Moistened clay characterised by its so-called argillaceous odour, its plasticity, and capability of being kneaded or puddled into layers impervious to water. Drying up of moist clay into hard opaque absorbent masses. Great shrinking of dry clay upon strong ignition, to leave hard, porous, unfused, anhydrous residue. Fusion even of pure clay in oxy-hydrogen blowpipe. Its fusibility much increased by presence of felspar, lime, magnesia, and ferrous oxide. Unburnt clay scarcely acted on by hydrochloric, but decomposed by strong sulphuric acid. Action of the sulphuric acid facilitated by a gentle, but prevented altogether by a strong, ignition of the

clay. Burnt or unburnt clay scarcely affected by aqueous caustic alkali, except under pressure. Its fusion however with caustic or carbonated alkali, to yield a completely soluble mixture of alkali-silicate and aluminate. Action of moist clay in withdrawing ammonia, alkalis, phosphates, organic matters, &c., from solution; whence one advantage of its presence in cultivated soils. Clay the basis of pottery of all kinds. In porcelain, the infusible clay mixed with materials yielding a fusible glass, as chalk, quartz, and felspar. In fine earthenware, the clay mixed with ground flints to diminish shrinking. Coarse earthenware made from various kinds of inferior clays and marls, *i.e.* mixtures of clay with chalk. Stoneware a semifused mixture of slightly marly clay with previously burnt and ground ware. Infusible fire-ware made from pure siliceous clay, with addition of previously burnt and ground ware to diminish shrinking. Pottery of different kinds glazed by being re-burnt, after receiving a coating of material yielding a more or less fusible glass. Fine glazing effected by a wash of ground felspar and quartz or flint. Coarser glazing, by the same materials with addition of glass and carbonate or oxide of lead. Stoneware glazed by introduction of common salt into the kiln. The salt volatilised and decomposed on the surface of the ware, through intervention of steam, oxide of iron, &c.:

$$2NaCl + H_2O + xSiO_2 = 2HCl + Na_2O.xSiO_2$$

Action of the blowpipe flame on most aluminium salts to leave a white, infusible, highly incandescent residue, acquiring a permanent bright blue colour when re-ignited after being moistened with nitrate of cobalt solution. Aluminium salts in solution recognised by their yielding with sufficiency of caustic potash or soda, a gelatinous precipitate of hydrated alumina, soluble in most acids and in excess of the precipitant. Precipitation of the same hydrate by sufficiency of ammonia, and of carbonate or sulphydrate of ammonium, potassium, and sodium; the precipitate being insoluble in excess of the precipitant. Precipitation

of alumina from its solution in potash or soda by neutralisation of solution with acid, or by addition thereto of carbonate, chloride, &c. of ammonium. Production of octahedral crystals of alum by dissolving precipitated alumina in acid-sulphate of potassium solution and evaporating down.

Conversion of normal into basic aluminium solutions by gradual addition thereto of caustic or carbonated alkali until occurrence of a permanent precipitate:

$$Al_2(SO_4)_3 + 2Na_2CO_3 + 2H_2O = 2Na_2SO_4 + Al_2SO_4(HO)_4 + 2CO_2$$

Abstraction of alumina from basic solution by vegetable fibre, with reproduction of normal salt. So prepared cloth said to be mordanted:

$$3Al_2SO_4(HO)_4 = Al_2(SO_4)_3 + 2Al_2(HO)_6 \text{ or } 4H_3AlO_3$$

Characteristic power of alumina and mordanted cloth to combine with different vegetal and animal colouring matters. Its employment in the production of *lakes*.

(74.) TIN.

Occurrence of tin in nature almost exclusively in form of stannic oxide SnO_2, known as tinstone or cassiterite. The ore in workable quantity found but in few localities, chiefly Cornwall, Malacca, Bolivia, and Australia. Its occurrence in alluvial deposits (stream-tin), and more commonly in veins of ancient rocks (vein-tin). Existence of some native tinstone in prismatic crystals, isomorphous with rutile TiO_2.

Crushed and washed ore first roasted to expel arsenic and sulphur, and then washed to separate iron as oxide, and copper as sulphate. Resulting stannic oxide smelted in reverberatory furnace with $\frac{1}{5}$ to $\frac{1}{8}$ part of charcoal or anthracite, and a little lime, to form slag with silica; and metal run into ingots. Purer tin separated from original ingots by liquation, the less pure and less fusible residue constituting block tin. Further purification of liquated portion by its fusion, agitation with damp

stakes, and subsidence. Metal from top half of pan most pure. Characteristic splitting up into prismatic fragments of fine tin heated short of its melting point and allowed to fall from a height. Chemically pure tin, in crystalline state, best got electrolytically by suspending bar of tin in stratum of dilute muriatic acid overlying stratum of concentrated stannous chloride solution.

Tin a lustrous, white, highly crystalline, fairly conductive metal, of sp. gr. 7·3, soft and extremely wanting in tenacity, ductile especially at 100°, and very malleable. Tin-foil obtainable of only ·001 inch thickness. Crackling of tin when bent, and its evolution of peculiar odour when handled. Its fusing point 230°. Latent heat of 1 kilo. of fused metal 14·25 units. Ebullition of tin at a white heat, and its very slight volatility at a full red heat. Its ready crystallisation by way of fusion, slow-cooling, and pouring away of unsolidified interior. Crystals referrible to square prismatic system. Crystalline character of ordinary tin made evident by washing the surface with dilute acids. Tin reduced to fine powder by constant agitation of the melted metal in a wooden box until solidified.

Bright tin scarcely affected by air and moisture, but tarnishable in air of towns. Its ready oxidation and combustion in air at temperatures above its melting point. Its decomposition of water at a full red heat, with evolution of hydrogen. Its similar combustibility in sulphur vapour and decomposition at a red heat of sulphuretted hydrogen. Its ready combination with the halogens. Curious indifference of tin to strongest nitric acid of sp. gr. 1·52. Its violent oxidation into compound $H_2Sn_5O_6.4Aq$, by nitric acid of sp. gr. 1·3, with reduction of the acid, partially to state of ammonia. Gradual solution of tin in strong muriatic acid, with formation of stannous chloride $SnCl_2$. Its solution in diluted nitro-muriatic acid, with formation of stannic chloride $SnCl_4$. Eventual production of stannic sulphate $Sn(SO_4)_2$, by action on tin of heated strong sulphuric acid, with liberation of sulphurous acid and sulphur. Tin oxidisable by fused caustic potash or soda, and readily by fused mixtures of alkali-nitrate with hydrate or carbonate.

On account of its permanency in air, tin frequently employed as a coating for more oxidisable metals iron and copper. In manufacture of so-called tin-plate, perfectly cleaned sheets of best charcoal iron immersed in bath of melted tallow, next in bath of tin melted under layer of tallow, then allowed to drain, and re-immersed in fresh bath of melted tin. Formation, in the process, of an iron-tin alloy. Copper utensils tinned by pouring on to them a little melted tin, frequently alloyed with small proportion of lead, and spreading it over the heated and perfectly cleansed copper surface with a piece of tow. Ordinary brass pins tinned by boiling them with granulated tin in a solution of cream of tartar, alum, and common salt.

Tin a constituent of numerous alloys. Non-separation of tin from fused alloys of tin with lead. Its partial separation from fused alloys of tin with copper; whence difficulty of obtaining large bronze castings of uniform composition, excess of tin accumulating at top, and excess of copper at bottom of casting.

Solder a variable mixture of lead and tin, from two parts lead and one part tin to two parts tin and one part lead. Presence of a little bismuth in some easily fusible solders. Common pewter an alloy of four parts tin with one part lead. Best pewter, or teapot-metal, an alloy of tin with lead, antimony, and bismuth (Queen's metal), or of tin with brass, antimony, and bismuth (Britannia metal).

Speculum metal a hard steel-white copper-tin alloy, containing about 33 per cent. of tin. Bell-metal, ordinary bronze, and gun-metal copper-tin alloys, containing respectively about 22, 15, and 10 per cent. of tin, with or without a small proportion of zinc, and in some cases of zinc and lead. Coinage bronze composed of 95 parts copper, 4 parts tin, and 1 part zinc. Specific gravity of copper-tin alloys greater than mean specific gravity of constituent metals. Alloys more fusible, less oxidisable, and very much harder than copper alone. Curious effect of sudden cooling to soften, and of slow-cooling or annealing to harden, copper-tin alloys.

Tin-amalgam of mirrors made by pouring mercury upon tin-

foil spread out on stone slab, sliding plate of glass gradually over the mercuriated foil, and pressing out excess of mercury by means of weights placed upon the glass. Presence in resulting amalgam of about 20 per cent. mercury and 80 per cent. tin.

Formation by tin of two series of compounds. Series of tetrad or stannic compounds typified by stannic chloride $SnCl_4$, and oxide SnO_2; and series of diad or stannous compounds typified by stannous chloride $SnCl_2$, and oxide SnO.

STANNIC COMPOUNDS.

Fluoride, SnF_4; evolved upon heating stannic oxide with oil of vitriol and fluor-spar, but not known as an isolated compound. Formed in solution by dissolving stannic oxide or hydrate in aqueous hydrofluoric acid. Product decomposed on evaporation into hydrofluoric acid and stannic oxifluoride:

$$SnF_4 + H_2O = SnF_2O + 2HF$$

Existence of numerous well-defined fluostannates isomorphous with corresponding fluosilicates, fluotitanates, &c. The potassium salt $K_2SnF_6.H_2O$, produced in lamellar crystals by saturating solution of potassium stannate with hydrofluoric acid and evaporating down.

Chloride, $SnCl_4$; made in solution by dissolving tin or stannous chloride in nitro-muriatic acid, avoiding excess of nitric acid; or by dissolving stannic hydrate in hydrochloric acid. Its recovery by evaporation of solution in hydrated rhombohedral crystals $SnCl_4.5Aq$. Made in anhydrous state by acting on heated tin with chlorine, or by distilling a mixture of pulverised tin and corrosive sublimate. Anhydrous stannic chloride a heavy mobile liquid, boiling at 120°, and fuming in moist air. Its dissolution of sulphur, phosphorus, iodine, and bituminous substances. Its miscibility with carbonic sulphide. Its combination with water attended by great extrication of heat and formation of a pasty mass known as butter of tin. Spontaneous formation of crystalline hydrate $SnCl_4.3Aq$, by exposing the

anhydrous compound to moist air. Solubility of stannic chloride in small quantity of water; but partial decomposition of the chloride by excess of water into stannic hydrate and hydrochloric acid. Curious precipitation of stannic hydrate from the chloride solution by addition of sulphate of sodium:

$$SnCl_4 + 4Na_2SO_4 + 4H(HO) = 4NaCl + 4NaHSO_4 + Sn(HO)_4$$

Free solubility of stannic chloride in aqueous hydrochloric acid, probably as the double salt H_2SnCl_6. Combination of stannic chloride with alkali-metal chlorides to form crystallisable salts, as K_2SnCl_6 and $(NH_4)_2SnCl_6$. Its combination also with tetrachloride of sulphur, pentachloride and oxichloride of phosphorus, &c. Its reaction with ammonia to form a volatilisable soluble mass of $SnCl_4.2NH_3$.

Bromide, $SnBr_4$; produced as a white, crystalline, fusible, volatile salt, by direct combination of bromine with tin or stannous bromide.

Iodide, SnI_4; formed with incandescence by heating tin-filings and iodine in a sealed tube. Yellowish red octahedrons melting at 146°, subliming considerably at 180°, and boiling at 295°.

Existence of various stannic methyl- and ethyl-halides, as:

$SnMe_4$	$SnMe_3I$	$SnMe_2I_2$	$SnMeI_3$	SnI_4
$SnEt_4$	$SnEt_3Cl$	$SnEt_2Cl_2$	$SnEtCl_3$	$SnCl_4$

Hydrates or acids. The compound $2H_2O.SnO_2$, or H_4SnO_4, or $Sn(HO)_4$, thrown down as a gelatinous precipitate, from stannic chloride by the action of alkali hydrates or carbonates, and from alkali stannates by addition of an acid. Ordinary stannic acid $H_2O.SnO_2$, or H_2SnO_3, or $SnO(HO)_2$, obtained by drying above precipitate in vacuo. Precipitate best formed from solution of the chloride, by addition of ammonia in excess or of calcium carbonate in deficit. The hydrate, whether moist or dry, soluble in dilute hydrochloric, sulphuric, and nitric acids; and in solutions of potash and soda. Its conversion into meta-stannic

acid by heat, and by ebullition of its sulphuric acid solution. Sodium stannate $Na_2SnO_3.3Aq$, made by fusing native tinstone with caustic soda, and in other ways. Its solubility in water, and crystallisation in hexagonal plates upon heating its saturated solution. Its use as a mordant. Potassium stannate $K_2SnO_3.4Aq$, a similarly prepared compound, crystallising in transparent rhombic prisms upon evaporation in vacuo of its aqueous solution. The alkali-stannates decomposed by all acids, including atmospheric carbonic acid.

Meta-stannic acid, $H_{10}Sn_5O_{15}$, or $H_2Sn_5O_{11}.4H_2O$, procured in hydrated state as a white, crystalloid, insoluble mass, by treating metallic tin with nitric acid of sp. gr. 1·42. Also precipitated by acidification of alkali meta-stannate solutions with dilute nitric acid. Composition of air-dried meta-stannic acid $H_2Sn_5O_{11}.9Aq$. Its capability of reddening moistened litmus paper. Composition of product dried at 100°, $H_2Sn_5O_{11}.4Aq$. Its conversion into ordinary stannic oxide by ignition.

Combination of meta-stannic acid with hydrochloric acid to form a compound insoluble in aqueous hydrochloric acid, but soluble in pure water, precipitable from the solution by addition thereto of hydrochloric acid, and decomposible into its constituents on ebullition of the solution. Meta-stannic acid insoluble in nitric acid. Its solubility in heated oil of vitriol. Solution capable of free dilution with water, but decomposed upon ebullition.

Meta-stannic acid soluble in solution of fixed caustic alkali, but not in aqueous ammonia, save in form of the freshly precipitated hydrate. Alkali-metal meta-stannates non-crystallisable salts, soluble in water to form strongly alkaline liquids, and precipitable therefrom by addition of caustic alkali and of most alkali-metal salts. Composition of alkali meta-stannates, dried at 130°, $K_2Sn_5O_{11}.4Aq$, and $Na_2Sn_5O_{11}.4Aq$ respectively. Their decomposition by ignition to leave residues decomposible by water into meta-stannic acid and caustic alkali. Meta-stannic acid recognised by formation of deep yellow stannous meta-stannate

$SnSn_5O_{11}.4Aq$, on its being moistened with stannous chloride solution.

Oxide, SnO_2; found native in form of tinstone or cassiterite, either massive or crystallised in extremely hard square prisms isomorphous with rutile. Made by heating the metal or its inferior oxide in a current of air; by igniting the several hydrates; and, in crystalline state, by passing mixed stannic chloride vapour and steam through red-hot tubes, &c. Amorphous stannic oxide a white powder, becoming temporarily brown yellow by heat, of sp. gr. 6·6, and of considerable hardness, whence its use under the name of putty powder for polishing. Its insolubility in all acids save the hydrofluoric. Formation of soluble stannates by its fusion with alkali hydrates or carbonates. Its easy reduction to the metallic state by ignition with charcoal, both on large scale and in reducing flame of mouth-blowpipe.

Sulphide, SnS_2; made in anhydrous state, as mosaic gold, by heating powdered tin-amalgam with sulphur and sal-ammoniac, at first gently and then to dull redness. Sal-ammoniac and cinnabar sublimed off, and stannic sulphide left as a gold-coloured flaky mass. Its evolution of sulphur by strong ignition. Its ready solubility in caustic alkali, forming a sulpho-stannate, &c. Its resistance to ordinary acids save the nitro-muriatic. Its absorption of chlorine to form a yellow crystalline compound SnS_2Cl_{12} or $SnCl_4.2SCl_4$. Hydrated stannic sulphide thrown down as a dull yellow precipitate by passing sulphuretted hydrogen through solution of a stannic salt, or by acidifying a dissolved sulpho-stannate. Precipitate dissolved by heated hydrochloric acid, in form of stannic chloride; and converted by nitric acid chiefly into meta-stannic acid. Its solubility in ammonia and in alkali hydrate, sulphydrate, and sulphide, in form of sulpho-stannate. Sodium sulpho-stannate $Na_2SnS_3.2Aq$ or $Na_2S.SnS_2.2Aq$, and ortho-sulpho-stannate $Na_4SnS_4.12Aq$ or $2Na_2S.SnS_2.12Aq$, obtainable, the former in yellow the latter in nearly colourless crystals.

STANNOUS COMPOUNDS.

Chloride, $SnCl_2$; left in anhydrous form upon heating a mixture of equal parts of tin-filings and corrosive sublimate. Also made by heating the hydrate in a closed crucible until fused, and distilling the fused mass from a glass retort. Anhydrous stannous chloride a white or greyish translucent mass, having a stony lustre and conchoïdal fracture. Its fusion at 250°, into an oily liquid, and ebullition below a red heat, with however some decomposition (into stannic chloride and metallic tin?). Its direct combination with chlorine, to form stannic chloride, attended with much extrication of heat.

Hydrated stannous chloride producible by dissolving the anhydrous compound in water; made by dissolving granulated tin in heated hydrochloric acid, preferably in copper vessels. Separation, upon cooling the hot concentrated solution, of colourless prismatic hydrated crystals $SnCl_2.2Aq$. Dehydration, with but little decomposition, of stannous chloride when heated in close vessels, to leave after much frothing, the anhydrous compound as an oily liquid. Its considerable decomposition however when heated in air, with evolution of hydrochloric acid and formation of an anhydrous oxichloride.

Hydrated stannous chloride soluble in small quantity of water; but partially decomposible by larger quantity, with precipitation of hydrated stannous oxichloride $Sn_2OCl_2.2Aq$:

$$2SnCl_2 \quad + \quad H_2O \quad = \quad Sn_2OCl_2 \quad + \quad 2HCl$$

Precipitation prevented by addition to the water of hydrochloric acid or sal-ammoniac. Crystals decomposed upon exposure to air with formation of the same oxichloride:

$$3SnCl_2 \quad + \quad O \quad = \quad Sn_2OCl_2 \quad + \quad SnCl_4$$

Aqueous stannous chloride constantly used in the laboratory as a reducing agent. Its reduction of gold, silver, and mercury salts to the metallic state; of ferric and cupric to the state of

ferrous and cuprous salts; and of yellow chromate to the state of green chromic salts. Its reaction with sulphurous oxide or acid, in presence of hydrochloric acid, to form stannous or stannic sulphide:

$$4HCl + 4SnCl_2 + SO_2 = 2H_2O + 3SnCl_4 + SnS$$

Combination of stannous chloride with chlorides of alkali-metals to form crystalline double salts as K_2SnCl_4, $(NH_4)_2SnCl_4$, &c. Probable existence of a similar hydrogen compound H_2SnCl_4.

Oxide, SnO; a black or brown powder of sp. gr. 6·7, made by heating stannous oxalate out of contact with air, by heating the hydrate in a current of nitrogen or carbanhydride, &c. Also, in crystalline state, by boiling the hydrate with aqueous caustic alkali in quantity insufficient to dissolve it. Stannous oxide permanent in air at ordinary temperatures; oxidisable, and even combustible, into stannic oxide when heated in air; and reducible to metallic state when heated with hydrogen or charcoal. Its solubility in most acids to form stannous salts. The hydrated oxide $H_2O.2SnO$ or $Sn_2O(HO)_2$, obtained as a white precipitate by decomposing stannous chloride with alkali carbonate. Compound rendered anhydrous by ebullition with water or deficit of aqueous alkali. Its gradual absorption of oxygen on exposure to air, to form stannic hydrate; and its action as a reducing agent. Its insolubility in ammonia, but solubility in fixed caustic alkali. Solution decomposed on ebullition, with formation of alkali stannate and metallic tin. Its dissolution in most acids, to form stannous salts, more facile than that of the anhydrous oxide.

Stannous stannate or sesquioxide of tin, $\overset{''}{Sn}\overset{''''}{Sn}O_3$ or Sn_2O_3, made by diffusing recently precipitated ferric hydrate in acid-free solution of stannous chloride and boiling. A slimy grey precipitate, completely soluble in ammonia, and also in hydrochloric acid to form a non-styptic and apparently colloid solution.

Sulphide, SnS; produced in anhydrous form by heating metallic tin with sulphur, as a fusible, leaden-grey, crystalline mass of sp. gr. 5·2. Produced in hydrated state as a dark brown

flocculent precipitate, by passing sulphuretted hydrogen through solution of stannous chloride. Precipitate insoluble in dilute, soluble in boiling hydrochloric acid, with evolution of sulphuretted hydrogen; insoluble in colourless alkali sulphydrate and sulphide, but soluble in yellow persulphide with formation of alkali sulpho-stannate:

$$K_2S_2 \ + \ SnS \ = \ K_2SnS_3 \ \text{or} \ K_2S.SnS_2$$

Solid tin compounds reducible before the blowpipe, without incrustation on the charcoal, to yield a bead of white malleable metal. The tin precipitates thrown down by sulphuretted hydrogen from stannous (dark brown) and stannic (pale yellow) solutions alike soluble in persulphide of ammonium, and re-precipitated (yellow) on acidification of the solution. Both precipitates insoluble in dilute, soluble in boiling hydrochloric acid, with formation of stannous and stannic chlorides respectively. Stannous chloride recognised by its reduction of gold and mercury salts. Stannic convertible into stannous chloride by addition of zinc, and dissolution in hydrochloric acid of any metallic precipitate at first thrown down.

(75.) Titanium.

Titanium found chiefly as titanic oxide TiO_2, in heteromorphous forms of rutile, brookite, and anatase; as ferrous titanite $FeTiO_3$, in ilmenite, menaccanite, &c.; as calcium titanate $CaTiO_3$, in perowskite; as calcium silico-titanate $Ca(Si\text{-}Ti)O_3$, in sphene or titanite; and as artificially produced titanous carbonitride Ti_5CN_4, or iron-slag titanium. Existence of titanium also in several rare minerals, and as a minute constituent of many iron-ores, clays, &c.

Titanium allied to tin and silicon by tetrad constitution and general habitude of its chief compounds; by the isomorphism of rutile TiO_2, with cassiterite SnO_2, and of titanium and silicon

with each other in titanite $Ca(Si\text{-}Ti)O_3$, and in the silico- and titano-fluorides K_2SiF_6 and K_2TiF_6; and by the existence of allotropic forms of hydrated titania, corresponding to those of stannic oxide. Ordinary titanic hydrate far more basic and earthy than ordinary stannic hydrate. Its combination with various acids to form titanic salts. Non-producibility of titanic sulphide in the moist way.

Metallic titanium procurable in prismatic crystals by heating sodium in vaporised titanic chloride; and, as a dark amorphous combustible powder, by heating potassium with potassio-titanic fluoride. Its solubility in hydrochloric acid with evolution of hydrogen, probably as titanous chloride $TiCl_2$.

TITANIC COMPOUNDS.

Fluoride, TiF_4; a fuming colourless liquid obtained by distilling a mixture of titanic oxide, fluor-spar, and oil of vitriol. Hydrotitanofluoric acid, $2HF.TiF_4$ or H_2TiF_6, made by treating titanic fluoride with water, or by dissolving titanic oxide in strong aqueous hydrofluoric acid. Existence of crystallisable titanofluorides of potassium K_2TiF_6, of ammonium $(NH_4)_2TiF_6$, &c. Unlike silica, titanic oxide not expelled from its compounds, when in presence of sulphuric acid, by their treatment with aqueous hydrofluoric acid.

Chloride, $TiCl_4$; made by heating mixture of titanic oxide and charcoal in current of chlorine. Heavy, fuming, volatile liquid, boiling at 135°, of vapour-density $96 = \frac{50 + 142}{2}$. Its direct combination with chloride and hydride of cyanogen, with tetrachloride of sulphur, and with chlorides of potassium and ammonium, &c. Its dissolution, when added little by little to cold water, in form of hydrated chloride of titanium, decomposible by evaporation into hydrated titania and hydrochloric acid.

Oxide, TiO_2. Its occurrence native in crystalline state, most abundantly in lustrous brownish dimetric prisms, of sp. gr. 4·25, as rutile. Also in acute octahedrons as anatase, and in right

rhombic prisms as brookite. Produced artificially, in amorphous state, by igniting the hydrate; and crystalline, by reaction of the vaporous chloride or fluoride with steam, &c. Titanic oxide fusible only in oxihydrogen blowpipe. Its insolubility in water, and in all aqueous acids except the hydrofluoric. Its gradual reaction with heated sulphuric acid to form titanic oxisulphate $Ti\left\{\begin{matrix}O\\SO_4\end{matrix}\right.$, left as a soluble pulverulent residue on driving off excess of acid. Its fusion with hydro-potassium sulphate into a clear yellow mass, soluble in water. Its reaction with fused potassium carbonate to form potassium titanate, separable as a white powder on washing away excess of alkaline carbonate, &c.

α-Hydrate, H_2TiO_3 or $H_2O.TiO_2$; produced by precipitating aqueous solution of distilled titanic chloride with ammonia. Or powdered rutile or ilmenite, after prolonged ebullition with hydrochloric acid to remove chief portion of iron, fused with excess of potassium carbonate. Resulting potassium titanate dissolved in cold hydrochloric acid, and crude titania precipitated from the solution by ammonia. Precipitate then digested successively in sulphide of ammonium to sulphurise iron, manganese, &c., and in sulphurous acid to dissolve away produced sulphides. Or the potassium titanate converted into titanofluoride by treatment with hydrofluoric acid, and titania precipitated by ammonia from solution of the recrystallised salt. A white powder, rendered temporarily yellow by heat, and anhydrous with vivid incandescence by stronger heat. Its solubility in very dilute acids. Its insolubility in solutions of fixed alkali, but withdrawal of alkali from the solutions as potassium or sodium titanate.

β-Hydrate, $x(H_2TiO_3$ or $H_2O.TiO_2)$; thrown down on boiling solutions of the α-hydrate in dilute acid, and by addition of hydrochloric or other acid to a boiled aqueous solution of distilled titanic chloride. Precipitate, after removal of adhering acid, soluble in much water, and reprecipitated on acidification. Its retention of water less forcible than that of the other variety. Its dehydration by strong heat unaccompanied by incandescence. Same compound formed by treating metallic titanium

with nitric acid of sp. gr. 1·25. Its analogy to meta-stannic acid.

Titanates. Alkali-metal compounds M'_2TiO_3, insoluble in water, soluble in dilute acids, made by fusing titanic oxide &c. with alkali hydrate or carbonate. Calcium salt $Ca''TiO_3$, found native in lustrous cubical crystals as perowskite. Ferrous salt $FeTiO_3$, found native in isomorphous association with very variable quantities of hæmatite Fe_2O_3, either massive or crystallised in rhombohedrons. Mineral known by very many names as ilmenite, iserine, menaccanite, &c. &c., titaniferous iron, titanic iron-sand.

Titanic salts. Occurrence of a titanic nitrate in crystalline laminæ; of titanic phosphate as a white gelatinous precipitate thrown down by sodium phosphate from aqueous titanic chloride; and of titanic basic sulphate as a white powder, made by dissolving titanic oxide in oil of vitriol and heating product to 180°.

TITANOUS COMPOUNDS.

Apparent formation by titanium of an inferior basic protoxide TiO, and corresponding chloride $TiCl_2$. Existence of intermediate sesqui-compounds Ti_2O_3 or $TiO.TiO_2$, analogous to $CaTiO_3$; also Ti_2Cl_6 or $TiCl_2.TiCl_4$ analogous to K_2TiCl_6; and Ti_2F_6 or $TiF_2.TiF_4$ analogous to K_2TiF_6. These sesqui-compounds producible by heating titanic oxide, chloride, and fluoride respectively with hydrogen gas, and in other ways. Production of blue or violet liquids by reducing solutions of titanic hydrate, in hydrochloric or other acid, with zinc, copper, &c. Production, by heating the double chloride of titanium and ammonium in ammonia gas, of a copper-coloured metallic-looking substance, titanous nitride Ti_6N_4, corresponding to Ti_6O_6. Occurrence in blast furnaces of analogous compound Ti_5CN_4, often in large masses, of metallic aspect, light copper colour, and sp. gr. 5·3. Substance made up of cubical crystals, hard enough to scratch glass. Its evolution of ammonia when heated with potash, and reduction of heated oxides of lead, copper, &c. with incandescence.

(76.) Zirconium.

Its chief source the silicate $ZrO_2.SiO_2$ or $ZrSiO_4$, known as zircon, jargon, or hyacinth. Its production in amorphous and crystalline forms by processes similar to those yielding corresponding forms of silicon. Amorphous zirconium made by passing chloride of zircon vapour over heated sodium, or by heating zircofluoride of potassium or sodium with either alkali metal:

$$K_2F_6Zr + Na_4 = 2KF + 4NaF + \overset{''''}{Zr}$$

A dull brown powder, extremely diffusible in pure, but readily subsiding from saline water; faintly lustrous after burnishing; scarcely attackable by acids, save the hydrofluoric; combustible in the air, at a heat below redness, to furnish zircon oxide or zirconia. Crystalline zirconium made by decomposing zircofluoride of potassium by ignition with excess of aluminium, cooling slowly, and dissolving away remaining aluminium from insoluble residue of separated zirconium.

$$3K_2F_6Zr + Al_4 + Al_x = 2(K_3F_3.Al_2F_6) + 3Zr.Al_x$$

Hard, brittle, crystalline laminæ, of sp. gr. 4·15, having colour and lustre of metallic antimony; combustible in air only at temperature of oxihydrogen flame, but combustible at a red heat in chlorine; soluble in hydrofluoric, and especially in nitro-hydrofluoric acid.

Fluoride, ZrF_4; obtained anhydrous by heating zirconia with hydrogen-ammonium fluoride $H(NH_4)F_2$, until expulsion of all ammonium salt. A white residue left, partially decomposed by water, soluble in aqueous hydrofluoric acid. Deposition from evaporated solution of the hydrate $ZrF_4.3Aq$, in small brilliant tabular crystals. Same solution formed by dissolving zirconia in aqueous hydrofluoric acid. Combination of other fluorides in various proportions with zirconium fluoride, to yield readily crystallisable zirco-fluorides isomorphous with silico- titano- and

stanno- fluorides of analogous composition. Complexity of only known sodium salt $5NaF.2ZrF_4$ (?). Most zirco-fluorides referrible to types $2MF.ZrF_4$, $MF.3ZrF_4$, and $4MF.ZrF_4$. Their solubility in aqueous hydrofluoric acid, and, save those of barium, strontium, and calcium, in water.

Chloride, $ZrCl_4$; formed by heating zirconium, or a mixture of zirconia and charcoal, in chlorine gas. A white sublimate, of vapour-density $115{\cdot}7 = \frac{89{\cdot}5 + 142}{2}$. Its solubility in water with rise of temperature to form the hydrated chloride, also producible by dissolving zircon hydrate in aqueous hydrochloric acid, and obtainable on evaporation in silky needles. Existence of several zircon oxichlorides, and of double zirco-chlorides of alkali-metal.

Oxide, ZrO_2; formed by combustion of the metal; usually made by gently heating the hydrate, and occasionally by strongly igniting the sulphate. Zirconia a white tasteless powder, insoluble in most aqueous acids. Its shrinking upon strong ignition, and occurrence in hard lumps, of sp. gr. 4·9, capable of scratching glass, infusible and intensely incandescent in oxihydrogen flame, difficultly soluble even in hydrofluoric acid, more soluble, however, in strong sulphuric acid. Zirconia also obtained, crystallised in quadratic prisms, of sp. gr. 5·7, isomorphous with tinstone and rutile, by fusing zirconia with borax in pottery furnace and exhausting mass with aqueous hydrochloric acid. Expulsion of water and carbanhydride from alkali hydrates and carbonates respectively, by their ignition with zirconia.

Hydrate; obtained in the first instance by fusing powdered zircons with sodium hydrate in silver crucible, or with a mixture of sodium carbonate and a little hydrate or nitrate in platinum crucible. Fused mass treated with hydrochloric acid, and the whole evaporated down to separate silica. Chloride of zirconium then extracted with water, and solution, if free from iron, precipitated at once with ammonia. If containing iron, nearly neutralised with sodium carbonate, boiled with sodium hyposulphite, and the precipitated zircon hyposulphite digested with ammonia. Probability of some zirconia at any rate, obtained from particular zircons, being a mixture of zirconia proper with some other earth as jargonia.

Hydrated zirconia, as obtained by addition of ammonia to zircon salts, a white gelatinous precipitate; drying up into a transparent mass, having a conchoidal fracture, and closely resembling similarly produced beryllia and alumina. Its differentiation from beryllia, however, by its insolubility in sal-ammoniac solution, and from beryllia and alumina by its insolubility in fixed caustic alkali. Its obstinate retention of some fixed alkali, when precipitated therewith. Formula of air-dried zircon hydrate $2H_2O.ZrO_2$ or H_4ZrO_4, corresponding to that of orthosilicic acid H_4SiO_4. Formula of product dried at 100° $H_2O.ZrO_2$ or H_2ZrO_3, corresponding to that of metasilicic acid H_2SiO_3. Conversion of both compounds into anhydrous zirconia by a heat short of redness. Corresponding zirconates made by fusing zirconia with basic oxides, hydrates, and carbonates. Formation from sodium carbonate of the two salts, Na_4ZrO_4 and Na_2ZrO_3, both decomposible by water. Formation from potassium hydrate of a compound entirely soluble in water. Zircon hydrate very slightly soluble in pure water to form an acid reacting liquid. The hydrate, when precipitated and washed in the cold, readily soluble in dilute acids. When precipitated or washed at boiling heat, soluble only in stronger acids. The normal nitrate, chloride, and sulphate, freely soluble salts having an astringent taste and acid reaction. Their combination with zircon hydrate to form basic salts. Reaction of zircon sulphate, $Zr(SO_4)_2$, with sulphate of potassium, in powder or concentrated solution, to form acid sulphate of potassium, and an insoluble compound of basic sulphate of zirconium with sulphate of potassium. Zirconium completely thrown down by neutralising the produced potassium acid sulphate with potassium carbonate, and washing collected precipitate with potassium sulphate solution. Carbonate, oxalate, hyposulphite, and phosphate of zirconium insoluble salts, producible by precipitation. But zircon carbonate soluble in excess of alkali-metal carbonate, especially of the hydro-carbonate; and zircon oxalate soluble in excess of ammonium oxalate. A zircon sulphide producible by ignition of zirconium in sulphur vapour, not in moist way.

(77.) Cerium, etc.

Existence of several rare metals, each forming a basic earthy oxide more or less analogous in character to lithia Li_2O, magnesia MgO, alumina Al_2O_3, and zirconia ZrO_2. Equivalent of each metal, or proportion by weight of each metal united with 35·5 parts of chlorine in the chlorides corresponding to above referred-to oxides, as follows: yttrium, 30·85 parts; erbium, 56·3 parts; cerium, 46·0 parts; lanthanum, 46·4 parts; didymium, 48·0 parts; and thorium, 57·87 parts. Entire want of positive knowledge as to atomic weight of each metal, and molecular formula of its chloride, oxide, &c. Conventional representation, however, of the several basic oxides as monoxides analogous to magnesia, MgO; and of the metals as diads, with the following symbols and atomic weights:

Y	Yttrium	61·7
Eb	Erbium	112·6
Ce	Cerium	92
La	Lanthanum	92·8
Di	Didymium	96
Th	Thorium	115·7

Yttrium and erbium found chiefly associated with each other as silicates, in gadolinite, $2YO.SiO_2$. Their occurrence also in yttro-titanite and yttro-tantalite. Cerium, lanthanum, and didymium found chiefly associated with each other as hydrated silicates, in cerite $2CeO.SiO_2.Aq$; as alumino-silicates, in orthite or allanite $\left.\begin{matrix}3CeO\\Al_2O_3\end{matrix}\right\}3SiO_2$; and as phosphates, in monazite or edwardsite $Ce_3(PO_4)_2$. Presence of some yttrium, &c. in most cerium minerals, and of some cerium, &c. in gadolinite and other yttrium minerals. Yttrium and cerium further met with together as fluorides, in yttro-cerite. Thorium found chiefly as hydrated silicate, in thorite or orangite $2ThO.SiO_2.xAq$; and said to be associated with cerium &c. in monazite. Yttrium-, cerium-,

thorium- minerals usually calcareous, ferruginous, and otherwise very complex in actual constitution. Above formulæ for the several minerals, typical only.

Thoria, yttria with erbia, and ceria with lanthania and didymia obtained by decomposing the native silicates with strong hydrochloric acid, evaporating to separate silica, precipitating with oxalic acid, and igniting resultant oxalates. Separation of above crude earths from one another, and from lime, magnesia, alumina, &c. effected by means of ammonia, oxalic acid, potassium sulphate, and sodium hyposulphite. Thorium salts precipitated by all four reagents; cerium &c. salts not by sodium hyposulphite; and yttrium &c. salts neither by sodium hyposulphite nor by potassium sulphate. The several metals obtained as lustrous powders by igniting the respective chlorides with potassium. The hydrated oxides formed as gelatinous precipitates, insoluble in caustic alkali, expulsive of ammonia from salammoniac solution, absorptive of carbonic acid from the air, and indifferent to sulphuretted hydrogen and soluble sulphides. The oxalates insoluble; the chlorides, nitrates, and sulphates readily soluble salts. Combination of the several sulphates with potassium sulphate to form sparingly soluble or insoluble double salts.

Yttrium and erbium separated from each other by repeated crystallising out of less soluble erbium- from more soluble yttrium nitrate. Yttria and yttrium salts colourless. Erbia and erbium salts rose-coloured. Emission spectrum of ignited erbia characterised by series of bright bands, and absorption spectrum of erbium solutions, by coincident dark bands. The potassio-sulphates of yttrium and erbium soluble, though much less so than the simple sulphates.

Production by ignition of cerous oxalate (and of the hydrate, carbonate, and nitrate), of a higher oxide Ce_3O_4. This ceroso-ceric oxide obtained free from lanthanum and didymium by digesting it with dilute, and afterwards with strong nitric acid. A yellowish white powder, becoming temporarily darker by heat, scarcely affected by ignition either in hydrogen or oxygen, in-

soluble in nitric acid; in its purified state almost insoluble in hydrochloric acid, but in its crude state dissolving readily therein, with evolution of chlorine and formation of the three mixed chlorides. Its solubility in strong sulphuric acid with formation of a yellow crystallisable ceroso-ceric sulphate. The hydrated oxide $Ce_3O_4.3Aq$, made by precipitating crude cerous chloride solution with potash, and passing excess of chlorine gas through the mixture. A bright yellow precipitate, readily soluble in sulphuric and nitric acids with formation of yellow ceroso-ceric salts; and soluble in hot hydrochloric acid with formation of colourless cerous chloride and evolution of chlorine:

$$Ce_3O_4 \quad + \quad 8HCl \quad = \quad 3CeCl_2 \quad + \quad Cl_2 \quad + \quad 4H_2O$$

Cerous oxide CeO, produced by igniting the oxalate or carbonate in current of hydrogen, as a greyish blue spontaneously oxidisable powder. The hydrate thrown down from cerous solutions by caustic alkali, as a gelatinous precipitate rapidly absorbing oxygen and carbonic acid. The sulphate $CeSO_4.3Aq$, made by dissolving cerous carbonate in sulphuric acid; reducing ceroso-ceric sulphate with sulphurous acid, &c. Salt freely soluble in cold water, partly precipitated by heat and redissolved upon cooling. Potassio-cerous sulphate $K_2Ce(SO_4)_2$, formed as a white powder by adding solid potassium sulphate to cerous sulphate solution, whether or not containing free acid. The double salt slightly soluble in water, insoluble in sulphate of potassium solution. Existence of a ceric fluoride Ce_2F_6, and of an oxifluoride Ce_2F_4O; but not of any ceric oxide.

Existence of but one set of lanthanum and of didymium salts respectively; but property of each metal to form, under suitable conditions, an ill-defined higher non-salifiable oxide, dissolving in hydrochloric acid with evolution of chlorine, and in sulphuric and nitric acids with evolution of oxygen. Lanthanum salts colourless, didymium salts of a rose colour, and both sets of compounds very similar in behaviour to analogous cerous compounds, save in the inferior oxidisability of the oxides and hydrates. The hydrates readily procurable by precipitation, and the oxides by

ignition of the hydrates in covered crucibles. Products readily soluble in mineral acids. Separation of lanthanum and didymium from each other very troublesome. With colourless lanthanum salt in excess, the anhydrous sulphates dissolved in ice-cold water, and resulting solution heated to 40°. Consequent precipitation of lanthanum- with but little didymium- sulphate. Process repeated several times. With coloured didymium salt in excess, the acid solution of mixed sulphates set aside in a warm place for some days. Consequent separation of didymium sulphate in large rhombohedral crystals, separable from small prisms of lanthanum sulphate mechanically. Exhibition by even very weak didymium solutions of an absorption spectrum, characterised by having a dark band in the yellow and another in the green.

Thorium oxide or thorina, ThO or $\text{Th}O_2$, allied to zirconia by its insolubility in acids after ignition, and by its crystallisation (after fusion with boric anhydride in pottery furnace) in quadratic prisms isomorphous with tinstone and rutile. Its remarkably high sp. gr. 9·4. Hydrated thorina procurable by precipitation of thorium salts with ammonia, as a well characterised base. Thoric chloride, $ThCl_2$ or $\text{Th}Cl_4$, formed as a white sublimate by ignition of mixed thorina and charcoal in current of chlorine. Its combination with alkali-metal chlorides to form double salts. Existence also of thorium fluoride, and of alkali-metal thorofluorides. Thorium oxalate, unlike zircon oxalate, insoluble in excess of ammonium oxalate solution.

Indium a recently discovered, and imperfectly examined, easily reducible metal, met with in small quantity in the zinc blende of Freiberg. Combination of 37 parts of indium with 35·5 parts of chlorine to form indium chloride. Atomic weight of indium and molecular formula of its chloride unknown, usually taken as 74 and $InCl_2$ respectively; possibly 111 and $InCl_3$, &c. A very soft, malleable, lead-coloured metal, of sp. gr. about 7·2, permanent in air and water, fusible and oxidisable at a red heat. Its hydrate thrown down as a white precipitate in-

soluble in excess of fixed or volatile alkali; and its sulphide as a yellow precipitate insoluble in acetic, but soluble in dilute mineral acids. Its chloride procurable in solution, and as a white crystalline sublimate. Spectrum of ignited indium salts characterised by two indigo lines, a very bright line more refrangible than the strontium-, and a fainter line less refrangible than the potassium-blue line. Violet coloration of the Bunsen flame by indium salts.

CHAPTER IX.

(78.) Arsenic Elements.

Arsenic, Antimony—Bismuth.

Vanadium—Niobium, Tantalum.

Metallic or semi-metallic elements associated with one another, and with phosphorus and nitrogen, by their common property of forming pentad compounds; in addition for the most part to inferior and, in some cases, better known triad compounds. Symbols, and atomic weights:

P	Phosphorus	31		V	Vanadium	51
As	Arsenic	75	76			
Sb	Antimony	122		Nb	Niobium	94
				Ta	Tantalum	182
Bi	Bismuth	210				

Special association of semi-metals arsenic, antimony, and bismuth with non-metallic phosphorus. Formation by each element of a volatile trichloride as $AsCl_3$, of a volatile triethide as $AsEt_3$, and, except by bismuth. of a gaseous trihydride as AsH_3, together with corresponding oxides, hydrates, &c. Formation also by each semi-metal of less-known pentad compounds, and more especially of oxides analogous to phosphoric anhydride P_2O_5, and of salts analogous to the phosphates $\overset{\prime\prime}{M}O.P_2O_5$ or $\overset{\prime\prime}{M}(PO_3)_2$, and $3\overset{\prime\prime}{M}O.P_2O_5$ or $\overset{\prime\prime}{M}_3(PO_4)_2$.

Vanadium distinguished from arsenic metals proper by various differences. Its resemblance to nitrogen in the seriation, composition, and to some degree in the properties of its oxides. Co-resemblance of the vanadiates and phosphates, and isomorphism of the minerals vanadite $Pb_5(VO_4)_3Cl$, and pyromorphite $Pb_5(PO_4)_3Cl$.

Save in the circumstance of their forming characteristic pentad compounds, niobium and tantalum but slightly associated with arsenic metals proper. Unlike other pentachlorides, those of niobium and tantalum, $NbCl_5$ and $TaCl_5$ respectively, volatile without decomposition or dissociation, to form gases or vapours having densities corresponding respectively to the halves of their received molecular weights.

(79.) Arsenic.

Arsenic met with in reguline state, associated with silver-glance, tinstone, &c. Also in the form of metallic arsenides as mangan-arsenide, and kupfer-nickel; of diarsenides as tesseral pyrites, white nickel pyrites, and smaltine; and of arsen-sulphides as mispickel, and nickel and cobalt blendes; compounds analogous in composition to, and frequently isomorphous with the corresponding sulphides:

FeS	FeS_2	
MnAs	$FeAs_2$	FeAsS
NiAs	$NiAs_2$	NiAsS
	$CoAs_2$	CoAsS

Further occurrence of arsenic in combination with sulphur as the disulphide or realgar As_2S_2, as the trisulphide or orpiment As_2S_3, and, in the form of different sulpharsenites, as red silver Ag_3AsS_3, tennantite $CuAsS_3$, the grey coppers, &c. Existence also of several metallic arseniates, more especially mimetine $Pb_5(AsO_4)_3Cl$, as somewhat rare crystalline minerals. Arsenic in small quantity very widely distributed in nature, and found as an impurity in many minerals, chiefly sulphuretted, and products obtained from them.

Arsenic usually obtained by heating mispickel in earthen tubes. Metal driven off and condensed as grey crystalline mass, in sheet-iron prolongations of the tubes:

$$4FeAsS = 4FeS + As_4$$

Occasionally, arsenious oxide heated with charcoal or black flux:

$$6C + 2As_2O_3 = 6CO + As_4$$

Metal from either source purified by resublimation, with rejection of more volatile or oxidised portion.

Arsenic a lustrous brittle metal, of sp. gr. 5·6 to 5·9, infusible under ordinary pressures, but volatile at 180°, and condensable in acute rhombohedrons isomorphous with those of antimony and tellurium, or in botryoidal crusts. Arsenic vapour, in quantity, of an orange-yellow colour. Its density 150 times that of hydrogen. Consequent molecular formula of arsenic As_4. Characteristic garlic-like odour of arsenic vapour, attributed to oxidation (?). Alleged existence of arsenic in two allotropic forms (Berzelius). Lustrous tin-white, denser, and more slowly oxidisable form obtained by condensing the metal at an elevated temperature in atmosphere of its own vapour, as when produced from mispickel. Steel-grey, crystalline, less dense, and more oxidisable variety furnished by deoxidation of arsenious oxide with charcoal. Tarnishing even of compact metal by its exposure to ordinary moist air. Its preservation in brilliant state by enclosure in water. Speedy and considerable oxidation of moistened pulverulent arsenic under exposure to air, with production of *fly-powder*. Oxidation of dry powder at 70° and upwards. Combustion of arsenic in air at below a red heat, with bluish-white flame and abundant evolution of opaque white smoke of arsenious oxide. Its brilliant combustion in oxygen. Its combination with chlorine, bromine, and iodine immediate, and often attended with combustion. Its combination at a gentle heat with sulphur, to form realgar or orpiment. Its conversion into arsenic acid by treatment with nitric or nitro-muriatic acid, and into an arseniate by deflagration with nitrate of alkali-metal. Its indifference to hydrochloric acid. Its dissolution in boiling potash ley and fused potash, with evolution of hydrogen and formation of arsenite and arseniate.

Reduction test for arsenic based on ready reducibility and volatility of metallic arsenic. Mixture of arsenical compound

with several times its own bulk of reducing flux (carbonate of sodium and charcoal) heated in small reduction tube. Metallic ring of arsenic obtained, characterised by its lustrous steel-grey colour, sometimes obscured by presence of a more volatile dark-coloured ring removable on gentle heating; by its volatility from one part of the tube to another; by its transformation, as a result of repeated volatilisations, into an iridescent crystalline ring of arsenious oxide; and by its yielding, after treatment with nitric acid, an evaporated residue of arsenic acid, recognisable by giving a brick-red precipitate with nitrate of silver.

Formation by arsenic of two well-defined series of compounds, a triad or arsenious series represented by arsenious hydride AsH_3, chloride $AsCl_3$, and oxide As_2O_3; and a pentad or arsenic series represented by arsenic acid $As\ddot{O}(HO)_3$, and anhydride As_2O_5.

Rarer manifestation also by arsenic of a diad or quasi-diad character, as in realgar AsS or As_2S_2, and in numerous arsenides and arsen-sulphides such as the nickel compounds $NiAs$, $NiAs_2$, and $NiAsS$.

Conversion of moist metallic arsenic, exposed to air, into a black powder, sometimes regarded as a definite suboxide As_2O. Decomposition of product, when gently heated out of access of air, into a sublimate of arsenious oxide and a residue of metallic arsenic.

ARSENIOUS COMPOUNDS.

Hydride, or arsenetted hydrogen, AsH_3; also known as arsine and hydrarsine. Gas made by decomposing metallic arsenides with water or acids:

$$3H_2O + AsNa_3 = 3NaHO + AsH_3$$
$$3H_2SO_4 + As_2Zn_3 = 3ZnSO_4 + 2AsH_3$$

Always produced during evolution of hydrogen in presence of arsenious and arsenic acids, or their salts:

$$H_6 + H_3AsO_3 = 3H_2O + AsH_3$$

In practice, hydrogen evolved by solution of zinc in sulphuric or hydrochloric acid, or by battery of several cells.

Hydrarsine an intensely toxic, alliaceous-smelling, colourless gas, condensable at $-40°$ into a transparent liquid, hitherto unsolidifiable. Solubility of the gas, at mean temperature, in about five times its volume of water. Perfect neutrality of the gas itself, and of its aqueous solution. Basylity, however, of its hydrocarbon derivatives as triethyl-arsine $AsEt_3$, &c. Its decomposition by a red heat, and slowly on exposure to sunlight, into metallic arsenic and hydrogen. Result of its explosion with oxygen, in excess and in deficit, to form water, together with arsenious oxide and reguline arsenic respectively:

$$O_6 + 2AsH_3 = 3H_2O + As_2O_3$$
$$O_3 + 2AsH_3 = 3H_2O + As_2$$

Combustion of mixed arsenetted hydrogen and hydrogen in air, with opaque bluish-white flame and abundant smoke of arsenious oxide. With access of air cut off, by depressing a piece of porcelain on the flame, greater part of arsenious oxide replaced by reguline arsenic deposited as a metallic stain upon the porcelain. Combustion of pure arsenetted hydrogen in free air, also accompanied by some separation of reguline arsenic. Arsenetted hydrogen decomposed by all oxidising agents as nitric acid, hypochlorous acid, &c. Action of chlorine instantaneous, attended with explosion or flame, and production of hydrochloric acid, together with arsenious chloride or metallic arsenic:

$$Cl_6 + AsH_3 = 3HCl + AsCl_3$$
$$Cl_6 + 2AsH_3 = 6HCl + As_2$$

Similar but less violent actions of bromine and iodine on arsenetted hydrogen (and, at a gentle heat, of sulphur and phosphorus) to combine with the hydrogen, and either to combine with or set free the arsenic. But action of sodium and zinc, at a moderate heat, to abstract arsenic and set free hydrogen. Action of caustic potash and soda, at a moderate heat, to form arsenide,

arsenite, and arseniate; with liberation of hydrogen both from the arsenetted hydrogen and caustic alkali:

$$3KHO + AsH_3 = H_6 + K_3AsO_3 \ (?)$$

Decomposition of most heavy metal salts by arsenetted hydrogen, with production of their several acids, and either metallic arsenide or metal and arsenious acid:

$$3CuSO_4 + 2AsH_3 = 3H_2SO_4 + Cu_3As_2$$

$$3H_2O + 6AgNO_3 + AsH_3 = 6HNO_3 + Ag_6 + H_3AsO_3$$

Marsh's test for arsenic based upon ready production of arsenetted hydrogen, and its decomposition, with separation of metallic arsenic, either by imperfect combustion or by simple ignition.

The arsenical stain, produced by depressing piece of porcelain or glass on flame of hydrogen contaminated with arsenetted hydrogen, identified by its metallic brilliancy, most characteristic on free surface of the stain; by its hair-brown colour, best seen on slight stains and near circumference of large stains; by its volatility on application of a heat below redness; by its solubility in a drop of bleaching powder solution; by its insolubility in a drop of cold persulphide of ammonium solution, but partial disappearance during evaporation of the drop to leave yellow residue of orpiment, with dark nucleus of metallic arsenic.

The arsenical deposit, produced by passing hydrogen contaminated with arsenetted hydrogen through glass tube heated to redness, identified by its brilliant steel-grey appearance; by its position beyond the heated portion of the tube; by its volatilisability from one part of the tube to another; by its conversion into arsenious oxide on sublimation in free air; and by its conversion into arsenic acid on treatment with nitric acid.

Arrest of any undecomposed arsenetted hydrogen by passage of the gas through nitrate of silver. Absolute freedom of hydrogen from arsenetted hydrogen shown by the unburnt gas not producing a flocculent black precipitate in nitrate of silver solution, or a black stain upon paper moistened with the solution.

Production under various circumstances, as in decomposition of sodium arsenide by water, &c., of an indefinite solid hydride of arsenic, in form of brown flocculi.

Arsenides. Their occurrence native; and production by adding arsenic to other metal in state of fusion, by reduction of arsenites, &c., and in various ways. Sodium and potassium arsenides dark-coloured opaque solids, decomposible by water, with evolution of arsenetted hydrogen gas, solid hydride of arsenic, and hydrogen. Basylous metal arsenides, as that of zinc, soluble in aqueous acids with evolution of arsenetted hydrogen. Majority of arsenides hard, brittle, fusible alloys, scarcely affected by mere ignition, but oxidisable in current of air with evolution of arsenious oxide. Their decomposition, by fusion with alkali-nitrate and carbonate, to form soluble arseniate and insoluble metallic oxide, as of iron, nickel, &c. Their reactions with chlorine, sulphur, &c., to form chloride or sulphide of arsenic, together with chloride or sulphide of other metal.

Metallic arsenides referrible to three principal types: $\overset{''}{M}_3As_2$, $\overset{''}{M}As$, and $\overset{''}{M}As_2$. Those pertaining to type $\overset{''}{M}_3As_2$, considered as derivatives of hydrarsine. Their production artificially by way of fusion, as of zinc and sodium arsenides $\overset{''}{Zn}_3As_2$ and $\overset{'}{Na}_3As$, for instance. Cupric arsenide $\overset{''}{Cu}_3As_2$, made by decomposing arsenetted hydrogen with cupric chloride, or arsenious chloride with copper filings. Cuprous arsenide $\overset{'}{Cu}_3As$, made by ignition of preceding compound, and found native as domeykite. A similar arsenide of nickel, $\overset{''}{Ni}_3As_2$, also found native. But the majority of native arsenides, including kupfer-nickel and white nickel pyrites, referrible to other two types. Frequent isomorphism of native arsenides $\overset{''}{M}As$, with sulphides $\overset{''}{M}S$; and of diarsenides $\overset{''}{M}As_2$, with arsen-sulphides $\overset{''}{M}AsS$, and disulphides $\overset{''}{M}S_2$. Thus smaltine $\overset{''}{Co}As_2$, and cobalt glance $\overset{''}{Co}AsS$, isomorphous with common iron pyrites $\overset{''}{Fe}S_2$; and mispickel, $\overset{''}{Fe}AsS$, with rarer form of iron pyrites known as marcasite.

Chloride, $AsCl_3$; producible by acting on metallic arsenic

with chlorine, the combination being often attended by combustion; or by distilling a mixture of metallic arsenic and corrosive sublimate. Best made by acting with sulphuric acid on mixed arsenious oxide and common salt, or on arsenious oxide dissolved in hydrochloric acid. In latter case arsenious chloride separated at once as a heavy layer:

$$As_2O_3 + 6HCl + xH_2SO_4 = 2AsCl_3 + \overbrace{3H_2O + xH_2SO_4}$$

A colourless, fuming, oily liquid, of sp. gr. 2·2, not solidifying at $-29°$, boiling at 132°. Its decomposition by excess of water, into arsenious oxide and hydrochloric acid holding some arsenious chloride in solution. Similar solution made by dissolving deficit of arsenious oxide in aqueous hydrochloric acid. Ready volatility of arsenious chloride, and consequently of arsenious oxide, in vapour of aqueous hydrochloric acid. Hence arsenic extracted from organic and other matters, in form suitable for submission to Marsh's or Reinsch's test, by distilling such matters once or twice to dryness with strong hydrochloric acid. Combination of arsenious chloride with the oxide to form semi-solid mass of arsenious oxichloride or chloride of arsenosyl:

$$AsCl_3 + As_2O_3 = 3AsOCl \text{ or } 3(AsO)Cl$$

Reinsch's test for arsenic performed by boiling clean metallic copper in dilute hydrochloric acid solution of arsenical compound. According to proportion of arsenic present, acquisition by the copper, in from two to fifteen minutes, of steel-grey coating of cupric arsenide:

$$2Cl_3As + Cu_6 = 3CuCl_2 + Cu_3As_2$$

Coated copper heated in reduction tube; with production of fixed cuprous arsenide, and volatilisation of metallic arsenic quickly oxidated into arsenious oxide, deposited as a ring of iridescent crystals upon cool part of the tube and capable of further examination. Process very delicate, and not impeded by presence of organic matter.

Bromide, $AsBr_3$; made by action of bromine on arsenic. A

white fibrous mass, melting at 25°, and boiling at 220°, very similar in its properties to the chloride.

Iodide, AsI_3; made by direct combination of iodine and arsenic. A lustrous, orange-brown, crystalline sublimate, soluble in and crystallisable from both disulphide of carbon and alcohol. Its solubility also in water, and deposition therefrom on evaporation in hydrated crystals.

Oxide, or anhydride, As_2O_3; familiarly known as white arsenic. Made by roasting different arsenical ores, and more particularly mispickel FeSAs. Product condensed in many-partitioned chambers or flues, in state of fine dust known as poison-flour. Its purification by resublimation, and condensation in the form of a translucent glass known as vitreous arsenic. Gradual change of vitreous arsenic, from circumference inwards, into opaque brittle mass known as porcellanous arsenic. Change facilitated by heat of 100°. Transparent also converted into opaque modification by simple pulverisation. Properties of the two modifications somewhat different. Condensation of sublimed white arsenic not only as above vitreous mass, but, by slow sublimation, in brilliant transparent octahedral crystals. Its deposition also from its solvents, water, strong ammonia, and dilute hydrochloric acid, in the same crystalline form. But condensation of sublimed white arsenic, at temperature intermediate between that furnishing vitreous mass, 400°, and that furnishing octahedral crystals, 200°, dimorphously in right rhombic prisms isomorphous with ordinary form of antimonious oxide. Same form of crystals occasionally deposited from solutions, especially from saturated solutions made at high temperatures under pressure.

Identity of crystalline and porcellanous varieties of white arsenic. Sp. gr. of vitreous arsenic 3·738, slightly higher than that of porcellanous or crystalline arsenic 3·689. Its solubility in water at mean temperature considerably greater. Eventual deposition of crystals from its solution. The deposition of crystals, on cooling solution of vitreous arsenic in aqueous hydrochloric acid, attended by a luminosity visible in the dark.

White arsenic, especially porcellanous variety, scarcely fusible on the small scale, save when heated under pressure. Its fusion when heated in sealed tubes, and condensation in vitreous state. Softening and considerable volatilisation of white arsenic heated, under ordinary conditions, to 200° and upwards. Specific gravity of vapour 198 times, instead of $\frac{150+48}{2} = 99$ times that of hydrogen. Consequent molecular formula of compound As_4O_6.

Characteristic non-adhesion of pulverulent white arsenic to water hot or cold. Considerable, but variously estimated, solubility of white arsenic in boiling water. Deposition of octahedral crystals on cooling the solution. Long continued retention of much more arsenic, in cooled and filtered liquid, than is dissoluble by mere agitation of white arsenic with water at the same temperature. Eventual slow separation of additional crystals from above solution. Much greater solubility of white arsenic both in aqueous hydrochloric acid and ammonia, than in water. Crystallisation of white arsenic upon cooling its warm saturated solution in either liquid. Production however of some arsenious chloride and ammonia arsenite, in the two cases respectively.

Solubility of arsenious oxide in fixed alkali, with formation of alkali arsenite. Its ready solubility in sulphide of ammonium to form a sulpharsenite, decomposible on evaporation so as to leave residue of orpiment. Its solubility in nitric acid, nitromuriatic acid, and chlorine water, with conversion into arsenic acid.

Reaction of arsenious oxide, gently heated in chlorine gas, to form arsenious chloride and a compound of arsenious with arsenic anhydride. Its ready reduction to metallic state by ignition with black flux, transmission over ignited charcoal, &c. Production of alkarsin or crude kakodyl $(CH_3)_4As_2$, by its distillation with acetate of sodium. Product recognised by its intolerable odour.

Acid, H_3AsO_3; and salts. Compound unknown in isolated state. The solution, obtained by boiling arsenious oxide in water and cooling, a styptic-tasting, acid-reacting liquid, neutralising caustic alkalis, and at a boiling heat decomposing carbonates with

effervesence. Formula of acid deduced from analogy, and existence of numerous well-defined arsenites $\acute{M}_3AsO_3$.

Aqueous arsenious acid slowly absorptive of oxygen from the air. Its reduction of gold salts to the metallic state; reduction of chromates and permanganates to state of chromic and manganous salts; and conversion of free chlorine, bromine, and iodine into their respective hydracids:

$$H_3AsO_3 \quad + \quad H_2O \quad + \quad I_2 \quad = \quad H_3AsO_4 \quad + \quad 2HI$$

In presence of arsenious acid, starch unaffected by free iodine, until complete conversion of the arsenious into arsenic acid.

Potassium arsenite KH_2AsO_3, made by boiling mixed potassium carbonate and arsenious oxide in water (Fowler's solution). Cupric arsenite $\overset{''}{Cu}HAsO_3$, thrown down as a green precipitate (Scheele's green), by adding an alkali arsenite to sulphate of copper, or arsenious acid to ammonio-sulphate of copper. Silver arsenite Ag_3AsO_3, thrown down as a yellow precipitate by adding an alkali arsenite to nitrate of silver, or arsenious acid to ammonio-nitrate of silver. Calcium arsenite $\overset{''}{Ca}_3(AsO_3)_2$, thrown down as a white precipitate by addition of arsenious acid to excess of lime-water. Its solubility in dilute acids including arsenious acid, and in ammoniacal salts.

Sulphide, or orpiment, As_2S_3; found native, both amorphous and crystallised in bright yellow oblique rhombic prisms, of sp. gr. 3·5. Produced in pure state by passing sulphuretted hydrogen through solution of arsenious chloride, or of the oxide dissolved in aqueous hydrochloric acid, and drying bright yellow precipitate. King's yellow, an impure arsenious sulphide containing more or less unchanged arsenious oxide, made by subliming a mixture of arsenious oxide and sulphur:

$$S_9 \quad + \quad 2As_2O_3 \quad = \quad 3SO_2 \quad + \quad 2As_2S_3$$

Orpiment readily fusible, and volatilisable without change in close vessels; combustible in air with a pale blue flame; reducible, with sublimation of metallic arsenic, by ignition with charcoal and

alkali carbonate; oxidisable into an arseniate by deflagration with nitre and alkali carbonate.

Orpiment insoluble in cold water; but, especially in freshly precipitated state, slowly dissolved to a considerable extent by boiling water, with evolution of sulphuretted hydrogen:

$$As_2S_3 \quad + \quad 6H_2O \quad = \quad 2H_3AsO_3 \quad + \quad 3H_2S$$

Probable intermediate production of sulpharsenious acid H_3AsS_3. Orpiment unaffected by hydrochloric acid; oxidisable by nitric or nitro-muriatic acid into mixture of arsenic and sulphuric acids; attackable by heated sulphuric acid with production of water and sulphurous and arsenious anhydrides. Its solubility in fixed and volatile alkali hydrate, sulphydrate, sulphide, and carbonate, and reprecipitation on acidifying resultant solutions. Solubility of recently precipitated orpiment in acid sulphite of potassium solution; with formation, upon ebullition, of potassium hyposulphite and arsenite, deposition of sulphur, and evolution of sulphurous anhydride.

Precipitation of orpiment by sulphuretted hydrogen made use of as a test for arsenic. Formation of distinct yellow precipitate in solutions containing only $\frac{1}{80,000}$ part of arsenious oxide. Precipitate characterised by its yellow colour, its insolubility in boiling hydrochloric acid, and its solubility in ammonia, carbonate of ammonia, and acid sulphite of potassium. Reduction of dried precipitate, heated with black flux, to furnish metallic ring; and its oxidation by fused nitre to furnish a soluble arseniate, decomposible by nitrate of silver with production of brick-red precipitate.

Sulphydrate, or sulpharsenious acid, H_3AsS_3; and sulpharsenites. Apparent production of sulpharsenious acid in solution by passage of sulphuretted hydrogen through aqueous arsenious acid. Liquid turned of a deep yellow colour, but not precipitated. Ordinary arsenious sulphide thrown down from the yellow liquid on addition thereto of hydrochloric acid, arsenic acid, &c.

$$2H_3AsS_3 \quad = \quad As_2S_3 \quad + \quad 3H_2S \ (?)$$

Formation of di-metal alkaline sulpharsenite in solution, by dissolving arsenious sulphide in alkali sulphydrate:

$$4KHS + As_2S_3 = 2K_2HAsS_3 + H_2S$$

On addition of alcohol, tri-metal salt precipitated leaving mono-metal salt in solution:

$$2K_2HAsS_3 = K_3AsS_3 + KH_2AsS_3$$

Alkali sulpharsenites unstable, gradually decomposing into dissolved sulpharseniates and precipitated inferior sulpho-salts of indefinite composition. Sulpharsenites of heavy metal procurable from alkali sulpharsenites by double decomposition. Several of them also found native as proustite, or light red silver Ag_3AsS_3, tennantite Cu_3AsS_3, &c.

Disulphide, or realgar, As_2S_2 or AsS. Found native in orange-red prismatic crystals isomorphous with those of orpiment. Producible in various ways; usually made, on large scale, by distilling common pyrites with arsenical pyrites:

$$2FeS_2 + 2FeAsS = 4FeS + As_2S_2$$

Artificial realgar in pure state, a ruby-red translucent mass. Commercial product an opaque, amorphous, dull red substance, more or less contaminated with arsenious oxide. Realgar readily fusible and volatile in close vessels, combustible in air, and very similar in its properties to orpiment. Its incomplete solubility, however, in caustic potash or soda. Its complete solubility in alkali sulphydrate and sulphide, with formation of sulpho-salts of uncertain composition.

ARSENIC COMPOUNDS.

Non-existence of any pentachloride, oxichloride, pentabromide, &c., of arsenic.

Oxide, or anhydride, As_2O_5; obtained by heating any form of arsenic acid to dull redness. An opaque, white, amorphous

mass; slowly absorptive of water to reproduce arsenic acid. Its very gradual deliquescence in moist air and dissolution in water, by reason of its conversion into arsenic acid. Its fusion at a red heat, with decomposition into arsenious oxide and oxygen. Its easy reduction to metallic state by ignition with charcoal, cyanide of potassium, &c.

Hydrate, or acid, H_3AsO_4; made by peroxidising arsenious oxide with nitric or nitro-muriatic acid and evaporating liquid product to syrupy condition:

$$2H_2O + 2HNO_3 + As_2O_3 = 2H_3AsO_4 + N_2O_3$$

Deposition from the cooled liquid, upon standing or agitation, of the hydrate $2H_3AsO_4.Aq$, in crystalline laminæ or prisms. Aqueous fusion of this product at 100°, with conversion into mass of needles constituting the acid H_3AsO_4. Both compounds, $2H_3AsO_4.Aq$ and H_3AsO_3, very deliquescent and dissoluble in water, the former with marked production of cold. Aqueous arsenic acid a strongly acid, metallic tasting, and, in its concentrated state, highly corrosive liquid, capable of expelling the more volatile acids from their salts, and of dissolving zinc and iron with evolution of hydrogen.

Action of arsenic acid as an oxidising agent, with self-reduction to the state of arsenious acid. Its reduction by sulphurous acid, gradual at ordinary temperatures, immediate at a boiling heat:

$$H_2SO_3 + H_3AsO_4 = H_2SO_4 + H_3AsO_3$$

Its decomposition, when boiled with strong hydrochloric acid, to furnish arsenious chloride and free chlorine:

$$H_3AsO_4 + 5HCl = 4H_2O + AsCl_3 + Cl_2$$

Sulphuretted hydrogen, for some time, without obvious effect upon aqueous arsenic acid. Gradual but complete deposition of the arsenic, however, in form of a yellow precipitate, sometimes considered as the pentasulphide As_2S_5, but seemingly a mixture of the trisulphide As_2S_3, with sulphur S_2. Same precipitate thrown

down on addition of hydrochloric acid to arsenic acid mixed with sodium hyposulphite solution:

$$2H_3AsO_4 + 5(Na_2S_2O_3.H_2O) = As_2S_3.S_2 + 5Na_2SO_4 + 8H_2O$$

Pure arsenic acid solution said to dissolve zinc and iron with evolution of arsenic-free hydrogen; in presence of hydrochloric or sulphuric acid, however, some arsenetted hydrogen always formed. But reduction of arsenic acid to state of arsenetted hydrogen, by solution of zinc in acid, much less satisfactory than reduction of arsenious acid. Hence advisability, in application of Marsh's test, of first reducing arsenic to state of arsenious acid by means of sulphurous acid. Arsenic acid highly poisonous, though apparently less so than, and as a consequence of its conversion into, arsenious acid. Its considerable use in the manufacture of aniline red, as an oxidising agent; and in calico-printing, as a mere acid, to effect the discharge of patterns printed with it upon a coloured ground, by immersion of the piece in weak bleaching liquor.

The arsenic acids corresponding to metaphosphoric and pyrophosphoric acids, producible only in the solid state. Their dissolution in water, with considerable development of heat and conversion into the tri-hydric or ordinary acid. Metarsenic acid $HAsO_3$, left as a white nacreous residue on heating common arsenic acid to 200°. Pararsenic acid $H_4As_2O_7$, deposited from dense mother-liquor in hard shining prismatic crystals on heating syrupy arsenic acid to 150°.

Arseniates. Close resemblance of these salts, mono-metallic MH_2AsO_4, di-metallic M_2HAsO_4, and tri-metallic M_3AsO_4, to the corresponding orthophosphates, in constitution, crystalline form, properties, and modes of production. Many of them found native as crystalline or semi-crystalline minerals. Occurrence of the native arseniate-chloride of lead $Pb_5\left\{\begin{matrix}Cl\\(AsO_4)_3\end{matrix}\right.$, or mimetine, crystallised isomorphously with apatite, in yellow hexagonal prisms.

All the alkali-metal arseniates soluble in water. The di-sodium, di-ammonium, and mono-potassium salts the best known.

Their production by neutralising aqueous arsenic acid with alkali carbonate, and evaporating. Crystallisation of the sodium salt Na_2HAsO_4, with 12 and 7 atoms of water. Alkali-metal arseniates also produced by deflagrating metallic arsenic, or arsenious oxide, or mixed arsenious oxide and alkali carbonate, with nitre.

Most other isolable arseniates insoluble in water. Ammonio-magnesian arseniate $\overset{\prime\prime}{Mg}(NH_4)AsO_4$, a white crystalline precipitate formed under the same conditions as the corresponding phosphate. Silver arseniate Ag_3AsO_4, a characteristic brick-red precipitate produced by addition of arsenic acid, or preferably of an alkali arseniate, to nitrate of silver solution:

$$Na_2HAsO_4 \quad + \quad 3AgNO_3 \quad = \quad Ag_3AsO_4 \quad + \quad 2NaNO_3 \quad + \quad HNO_3$$

Cupric arseniate $\overset{\prime\prime}{Cu}HAsO_4$, produced as a flocculent pale blue precipitate by addition of alkali arseniate to cupric sulphate, or of arsenic acid to ammonio-cupric sulphate solution.

Arseniates of heavy and earth-metals soluble in mineral acids, including arsenic acid, with apparent conversion into mono-metallic or super-acid salts as AgH_2AsO_4, $\overset{\prime\prime}{Cu}H_4(AsO_4)_2$, &c. Production of a bright yellow precipitate on adding molybdate of ammonia in excess to the nitric acid solution of arsenic acid, or of any arseniate, and gently warming. Precipitate exactly similar to that produced under the same circumstances in phosphate solutions.

Sulphide, As_2S_5. The precipitate eventually thrown down by sulphuretted hydrogen from aqueous arsenic acid, a mixture of arsenious sulphide soluble, and of free sulphur insoluble, in dilute ammonia. Formation, on acidifying the solution of an alkali sulpharseniate, of true arsenic sulphide, as a bright yellow precipitate completely soluble in ammonia:

$$2Na_2HAsS_4 \quad + \quad 4HCl \quad = \quad 3H_2S \quad + \quad As_2S_5 \quad + \quad 4NaCl$$

Arsenic sulphide usually made by heating orpiment with sulphur. A bright yellow fusible mass, volatilisable without change out of contact with air, and soluble in alkali sulphide, sul-

phydrate, hydrate, and carbonate, with formation of sulpharseniates.

The sulpharseniates unimportant salts. Those of the alkali-metals difficultly crystallisable compounds, producible as above; also by treating the corresponding oxy-arseniates with sulphuretted hydrogen; and in other ways. Their solubility in water to form yellow liquids, giving precipitates of heavy metal sulpharseniate with solutions of heavy metal salts.

Compounds of arsenic, in solid state, recognised by their affording sublimates of reduced metal when heated in narrow glass tubes with carbonate of sodium and charcoal. Compounds in acidified solution recognised, after treatment if necessary with sulphurous acid, by Marsh's and Reinsch's tests; and by their giving with sulphuretted hydrogen a yellow precipitate of arsenious sulphide, insoluble in boiling hydrochloric acid, soluble in nitric and nitro-muriatic acids, and soluble in carbonate of ammonium.

(80.) Antimony.

Antimonious sulphide Sb_2S_3, or stibnite, by far the most abundant ore of antimony. Existence however, in nature, of numerous other antimony minerals, including the metal Sb_x; its combination with nickel or breithauptite NiSb; its combination with silver or dicrasite Ag_6Sb; its teroxide or valentinite Sb_2O_3; its tetroxide or cervantite Sb_2O_4; and very many sulphantimonites (*q.v.*), such as myargyrite $AgSbS_2$, dark-red silver Ag_3SbS_3, &c.

Antimony usually obtained by the so-called martial process. Bundle of scrap-iron thrust into mass of melted antimonious sulphide. Consequent transfer of sulphur to the iron, so as to form slag of ferrous sulphide overlying the reduced antimony:

$$Sb_2S_3 + Fe_3 = Sb_2 + 3FeS$$

Or antimonious sulphide roasted, so as to drive off greater part

of its sulphur as sulphurous anhydride, leaving residue of oxide with some oxisulphide, afterwards smelted with charcoal and a little carbonate of sodium.

Commercial antimony purified by fusing a mixture of the powdered metal with $\frac{1}{8}$ of its weight of carbonate of sodium and $\frac{1}{16}$ of its weight of antimonious sulphide. Most foreign metals thereby sulphurised and dissolved in the slag. Resulting metal again powdered, and fused once or twice with carbonate of sodium and a little nitre to remove arsenic by its conversion into arseniate.

Pure antimony obtained for experimental purposes by igniting oxichloride of antimony or antimoniate of sodium with mixed carbonate of sodium and crude tartar, washing the crushed button with water to remove reduced alkali-metal, and remelting the washed antimony with carbonate of sodium and a little nitre or pre-formed antimony oxide.

Reduction of antimony compounds, heated with carbonate of sodium on charcoal before the blowpipe, to yield a bead of brittle metal with abundant bluish-white incrustation. Reaction made use of as a test for antimony.

Antimony a lustrous bluish-white metal, of sp. gr. 6·6 to 6·8, brittle and highly crystalline. Its occurrence native in rhombohedral crystals, isomorphous with those of arsenic and tellurium. Its production in cup of rhombohedral crystals by fusion, slow cooling, and eventual pouring away of central fluid metal from solidified exterior. Difficulty of crystallisation in proportion to purity of the metal. Antimony fusible at 450°, capable of distillation at a white heat, and freely volatilisable at a full red heat. Its indifference at ordinary temperatures to action of dry or moist air. Its rapid oxidation when heated above its melting point. Its combustion in oxygen, and less vividly in air, at a full red heat. Its ready attackability by the halogens. Spontaneous combustion even of the finely powdered metal in chlorine gas. Antimony readily attackable also by nitric acid, with formation of antimonic hydrate. Its indiffer-

ence to dilute sulphuric acid, but reaction at a moderate heat with the strong acid to furnish antimonious sulphate. Its considerable resistance to action of hydrochloric acid, but ready dissolution in nitro-muriatic acid with formation of antimonious or antimonic chloride. Its solubility in solutions of alkali polysulphide. Its deflagration with nitre to produce antimoniate of potassium.

Antimony deposited, in crystalline state, by electrolysis of dilute antimonial solutions. Its deposition also, in peculiar soft amorphous state, by electrolysis of concentrated solutions, as of tartar-emetic in antimonious chloride (Gore). Such metal characterised by its lustrous, dark grey, almost black colour; by its low sp. gr. 5·7 to 5·8; and by its undergoing, when heated or sharply struck, a sort of explosion attended by a considerable manifestation of heat, an evolution of some retained antimonious chloride, and a restoration of the metal to its ordinary condition.

Formation by antimony of two well-defined series of compounds, a triad or antimonious series typified by antimonious chloride $SbCl_3$, and a pentad or antimonic series typified by antimonic chloride $SbCl_5$. Existence also, in addition to the two corresponding oxides, Sb_2O_3 and Sb_2O_5 respectively, of an intermediate antimonoso-antimonic oxide, Sb_2O_4 or $\overset{'''}{Sb}\overset{v}{Sb}O_4$.

ANTIMONIOUS COMPOUNDS.

Hydride, H_3Sb; also known as antimonetted hydrogen, stibine, or hydro-stibine. A colourless, inodorous, insoluble gas, obtainable only in admixture with hydrogen. Best produced by dissolving antimony-zinc alloy in dilute hydrochloric or sulphuric acid:

$$Zn_3Sb_2 \quad + \quad 6HCl \quad = \quad 2H_3Sb \quad + \quad 3ZnCl_2$$

Decomposition of antimonial solutions, in presence of zinc and acid, with partial precipitation, partial hydrogenation of reduced

antimony. Antimonetted hydrogen gas decomposed below a red heat into antimony and hydrogen; combustible in free air with bluish-white flame and opaque smoke of antimonious oxide. With access of air cut off, by depressing a piece of porcelain on to the flame, hydrogen only burnt and antimony deposited on the porcelain as a sooty metallic stain. Oxidation of antimonetted hydrogen by strong nitric acid with deposition of antimonic oxide. Its action upon nitrate of silver solution to produce a flocculent black deposit, not of metallic silver as with arsenetted hydrogen, but of silver antimonide Ag_3Sb. Existence of organic derivatives of antimonetted hydrogen, as methyl- and ethyl- stibine, Me_3Sb and Et_3Sb respectively.

Ready production and decomposition of antimonetted hydrogen the basis of Marsh's test for antimony. Antimonial stain, produced on glass or porcelain by imperfect combustion of the gas, differentiated from similarly produced arsenical stain by its general want of lustre; by its smoky black colour; by its non-volatility save at a red heat; by its insolubility in solution of bleaching-powder; by its speedy solubility in yellow sulphide of ammonium to form a solution yielding, on evaporation to dryness, an orange stain of antimonious sulphide; and by its leaving, after treatment with nitric acid and evaporation to dryness, a white residue unaffected by nitrate of silver, but turned orange by sulphuretted hydrogen. Antimonial deposit, produced by heating current of antimonetted hydrogen transmitted through glass tube, characterised by its position at the exact spot subjected to heat; by its want of volatility; by its oxidation without transference when heated in current of air; and by its conversion, when heated in sulphuretted hydrogen, into an orange deposit of antimonious sulphide, disappearing immediately in current of hydrochloric acid.

Antimonides. Combination of antimony with other metals to form both definite antimonides, and alloys of variable composition. Antimonides found native, formed by direct union of constituent metals, and by reactions of antimonetted hydrogen on salts of different metals. Antimonides mostly

referrible to two principal types, $\acute{M}_2Sb$ and $\acute{M}_3Sb$ respectively, but other varieties also met with. Nickel antimonide $\ddot{N}iSb$ or $\ddot{N}i_2Sb_2$, found native as breithauptite, crystallised in thin hexagonal plates. Zinc antimonide $\acute{Z}nSb$ or $\acute{Z}n_2Sb_2$, made by fusing the two metals together. Its crystallisation in broad rhombic plates. Another zinc antimonide $\acute{Z}n_3Sb_2$, made by fusing antimony with greater proportion of zinc. Its crystallisation in large acicular prisms belonging to the right prismatic system. Decomposition of boiling water, with evolution of hydrogen, by both compounds, the former slowly, the latter rapidly. Different crystalline forms of the two alloys curiously unaffected by considerable variations in the proportions of their constituent metals. Silver antimonide Ag_3Sb, produced as a black flocculent precipitate by transmission of antimonetted hydrogen gas through nitrate of silver solution:

$$H_3Sb \quad + \quad 3AgNO_3 \quad = \quad Ag_3Sb \quad + \quad 3HNO_3$$

Another silver antimonide Ag_6Sb, and occasionally Ag_4Sb, found native as dicrasite. A potassium antimonide of variable composition, containing from 10 to 12 per cent. of potassium, made by strongly igniting tartar-emetic mixed with nitre in deficit, or powdered metallic antimony mixed with cream of tartar. Its violent action on water to furnish hydrogen and caustic potash. Its use in the production of ethyl-stibine Et_3Sb, &c.

Ordinary type-metal an alloy of lead with 20—25 per cent. of antimony. Alloy fitted for type-founding by its considerable expansion on solidification; and for impression, by wanting the softness of its one and brittleness of its other constituent. Introduction of tin and occasionally of bismuth in some varieties of type-metal. White metal for machinery bearings an alloy of tin, or of tin and lead, with antimony. Best pewter or teapot metal an alloy of tin and lead, or of tin and brass, with antimony.

Chloride, $SbCl_3$; producible in many ways, as by heating

antimony or antimonious sulphide with deficit of chlorine; by dissolving antimonious sulphide in hydrochloric acid, or metallic antimony in nitro-hydrochloric acid, and evaporating down; by distilling metallic antimony or antimonious sulphide with corrosive sublimate; &c. Distilled antimonious chloride a soft, translucent, yellowish solid, known to the older chemists as butter of antimony. Its fusion at 72°, and ebullition at 223°. Its fuming and deliquescence in moist air; and considerable volatilisation in vapour of boiling aqueous hydrochloric acid. Its dissolution unchanged in hydrochloric acid, and in small quantity of water. Its decomposition by excess of water, with precipitation of the oxichloride $Sb\ddot{O}Cl$. Its combination with alkali-metal chlorides to yield crystallisable double salts; and with ammonia to form the compound $NH_3.SbCl_3$.

Oxichloride, $Sb\ddot{O}Cl$; formed, a sabove described, by action of water on antimonious chloride, or on its solution in not too great an excess of hydrochloric acid:

$$SbCl_3 \quad + \quad H_2O \quad = \quad Sb\ddot{O}Cl \quad + \quad 2HCl$$

A dense white precipitate, easily fusible, and solidifiable on cooling into a translucent crystalline mass. Its ready solubility in cream of tartar, tartaric acid and hydrochloric acid. Its decomposition by prolonged action of water, and especially boiling water, with gradual removal of chlorine, so as ultimately to leave antimonious oxide.

Bromide, $SbBr_3$; made by careful addition of antimony to bromine, and distillation of the product. A white crystalline deliquescent mass, decomposible by water to yield the oxibromide SbOBr. Antimonious iodide SbI_3, a similarly produced and reacting brown-red compound.

Oxide, Sb_2O_3; found native as valentinite in white shining orthorhombic prisms; and more rarely as senarmontite in regular octahedrons. Its production, in amorphous state and in both crystalline forms, by slow combustion of antimony in current of air. Its usual production as a white crystalline precipitate by

pouring solution of antimonious chloride into boiling carbonate of sodium solution.

A white or greyish-white powder, becoming temporarily yellow when heated. Its fusion and volatilisation in close vessels to yield a crystalline sublimate. Its quasi-combustion when heated to redness in air, with production of the tetroxide. Its oxidation also by strong nitric acid. Its ready reduction to metallic state by ignition with hydrogen, charcoal, &c. Its slight solubility in water; and free solubility in hydrochloric acid to form solution of antimonious chloride. Its ready solubility also in tartaric acid and cream of tartar.

Antimonious and arsenious oxides isodimorphous, the ordinary form of the one compound corresponding with the rare form of the other.

Hydrate, $HSbO_2$ or $H_2O.Sb_2O_3$; produced by addition of antimonious chloride to excess of cold, or but slightly warm, carbonate of sodium solution. Its dehydration at a gentle heat. Its solubility in fixed caustic alkalis to form unstable antimonite solutions, as of $KSbO_2$, decomposible by ebullition or evaporation with deposition of crystalline antimonious oxide. Characteristic reduction of chloride of gold and nitrate of silver by alkaline antimonious solutions, with production of black precipitates insoluble in ammonia. Blackening of antimonious hydrate and of the finely divided amorphous oxide, when moistened with ammonio-nitrate of silver.

Oxisulphide, Sb_2S_2O; found native as red antimony-ore in bright red fibrous crystals, having a stony lustre. So-called vermillion of antimony, made by adding antimonious chloride to excess of sodium or calcium hyposulphite and boiling, said to have the same composition as the natural compound. Crocus of antimony and glass of antimony indefinite oxisulphides produced by imperfect roasting of the native sulphide, by fusion of the sulphide with the oxide, &c. The name crocus also applied to antimony smelters' scoriæ, containing sulphantimonite of sodium.

Sulphide; Sb_2S_3. Its existence in crystalline steel-grey, and

amorphous orange-red states. The crystalline variety found native as stibnite or grey antimony-ore in many parts of the world, and extracted from its gangue by simple fusion. Its contamination with other sulphides as of lead, copper, iron, and arsenic. Crystalline antimonious sulphide produced artificially by fusing any variety of the amorphous sulphide; and by heating antimony or its oxides with sulphur:

$$Sb_2O_4 \quad + \quad S_5 \quad = \quad Sb_2S_3 \quad + \quad 2SO_2$$

Opaque brittle masses, made up of acicular crystals (orthorhombic prisms), of sp. gr. 4·5, steel-grey colour and strong metallic lustre. Melting of compound at a red heat, its volatilisation at a white heat, ready oxidation when heated in a current of air, and desulphuration when strongly heated with iron, hydrogen, charcoal, &c. Its solution in hydrochloric acid, with formation of antimonious chloride and evolution of sulphuretted hydrogen:

$$Sb_2S_3 \quad + \quad 6HCl \quad = \quad 2SbCl_3 \quad + \quad 3H_2S$$

Its ready attackability by chlorine and bromine, and by strong nitric and sulphuric acids. Its deflagration with nitre to form sulphate and antimoniate of potassium. Its solubility in boiling alkali hydrate, sulphide, sulphydrate, and carbonate.

Amorphous antimonious sulphide made by suddenly cooling the native sulphide, fused at a high temperature. An amorphous mass, of sp.gr. 4·15. Its vitreous lustre, conchoidal fracture, dark red colour, and reducibility to an orange-brown powder. Hydrated antimonious sulphide thrown down as a bright orange precipitate, by action of sulphuretted hydrogen on acidified antimonious solutions, and by acidification of alkali sulphantimonite solutions. Its dehydration at a moderate heat, without alteration of colour. Its fusion at a red heat, and solidification on cooling as the grey crystalline sulphide.

Sulphantimonites. The best known native sulphantimonites formulated below. Frequent greater or less isomorphous

replacement, in the several crystalline minerals, of antimony by arsenic, and of different basic metals by one another:

Meta-salts	$Ag_2S.Sb_2S_3$	or	$AgSbS_2$	Myargyrite
	$Cu_2S.Sb_2S_3$	,,	$CuSbS_2$	Wolfsbergite
	$PbS.Sb_2S_3$	,,	$Pb(SbS_2)_2$	Zinkenite
	$FeS.Sb_2S_3$	,,	$Fe(SbS_2)_2$	Berthierite
Ortho-salts	$3Ag_2S.Sb_2S_3$	,,	Ag_3SbS_3	Pyrargyrite
	$Cu_2S.2PbS.Sb_2S_3$	,,	$\acute{C}u\acute{P}bSbS_3$	Bournonite
	$3PbS.Sb_2S_3$	,,	$Pb_3(SbS_3)_2$	Boulangerite
Para-salts	$2PbS.Sb_2S_3$	,,	$Pb_2Sb_2S_5$	Plumosite
	$2(\acute{C}uFe)S.Sb_2S_3$	,,	$(\acute{C}uFe)_2Sb_2S_5$	Panabase

Solubility of antimonious sulphide in alkali sulphide or sulphydrate to form a sulphantimonite solution. Its solubility also in caustic alkali to form an indefinite oxisulphantimonite solution. Dissolution of excess of antimonious sulphide in produced liquid at boiling heat, and its deposition on cooling as kermes. Precipitation on acidifying the liquid, before or after its deposition of kermes, of amorphous antimonious sulphide, in latter case of a bright orange colour, whence its name of golden sulphuret. Frequent presence of some antimonious oxide or oxisulphide in the several precipitates.

Salts. Reactions of antimonious oxide and hydrate with various acids to form both normal and basic or oxi-salts. Predescribed chloride $SbCl_3$, and the sulphate $Sb_2(SO_4)_3$, the only important normal salts, known in isolated state. The latter made by heating metallic antimony or antimonious sulphide with strong sulphuric acid. A white mass, soluble in excess of acid and crystallising therefrom in small needles. Its decomposition by water with formation of various insoluble basic salts. Antimonious hydrate and the precipitated oxide soluble in strong nitric acid, and resulting solution decomposed by water with precipitation of a basic nitrate, convertible into the oxide by washing.

Best known basic salt of antimony the potassio-tartrate, or

tartar-emetic. Solubility of antimonious oxide, oxichloride, oxisulphate, &c. in, and their precipitation prevented by presence of, tartaric acid and cream of tartar. Tartar-emetic represented as a basic potassio-tartrate of triad antimony, analogous to the oxichloride; or, more frequently, as a potassio-tartrate of the monad radical antimonyl SbO :

$$\overset{'''}{Sb}\begin{cases}\overset{''}{O}\\Cl\end{cases} \quad \text{or} \quad (SbO)'Cl; \qquad \overset{'''}{Sb}\begin{cases}\overset{''}{O}\\K\overline{T}\end{cases} \quad \text{or} \quad (SbO)K\overline{T}$$

Its production by reaction of antimonious oxide and cream of tartar:

$$Sb_2O_3 \quad \text{or} \quad (SbO)_2O \quad + \quad 2HK\overline{T} \quad = \quad H_2O \quad + \quad 2(SbO)K\overline{T}$$

Salt crystallisable, as $2(SbO)K\overline{T}.Aq$, in orthorhombic octahedrons and tetrahedrons. Its aqueous solution not disturbed by alkalis, but decomposed on acidification with mineral acids to yield white precipitates, soluble in excess of mineral acid and in tartaric acid.

In absence of tartaric acid or a tartrate, acid antimonious solutions characteristically decomposible by water to yield white precipitates, distinguishable from similar bismuth precipitates by their solubility in tartaric acid, and their orange coloration by sulphuretted hydrogen.

Acid antimony solutions, whether or not containing tartaric acid, &c., further recognised by their giving with sulphuretted hydrogen an orange precipitate, soluble in sulphide of ammonium and in ammonia, but not soluble in carbonate of ammonium. Precipitate also soluble in boiling hydrochloric acid to form a solution of antimonious chloride,—after sufficient evaporation, precipitable by water as above.

Acid antimonial solutions, whether or not containing tartaric acid, &c., reducible by the more basylous metals, especially zinc, tin, and copper; and slowly oxidisable by auric chloride with precipitation of metallic gold. In presence of zinc and acid, dissolved antimony not only reduced but partially hydrogenised,

so as to be recognisable by Marsh's test. Precipitation of antimony on metallic tin as a black pulverulent deposit, or from very dilute solutions as a black stain. Reinsch's test for antimony based on reduction of dilute antimonial solutions, acidulated with hydrochloric acid, by their ebullition with clean copper foil. Acquisition by the foil of a characteristic, lustrous, purple coating of copper antimonide; yielding up its antimony, upon ebullition of the foil with dilute potash under exposure to air, to form a solution precipitable, after acidification with hydrochloric acid, by sulphuretted hydrogen.

ANTIMONIC COMPOUNDS.

Chloride, $SbCl_5$; made by direct action of chlorine on antimony or antimonious chloride. A yellow fuming liquid, solidifying at 0° into a crystalline mass. Its decomposition by ebullition into antimonious chloride and free chlorine; whence its use as a chlorinating agent, to effect the conversion of carbonous oxide into phosgene for instance. Its reaction, with a small quantity of water, to produce white deliquescent crystals probably of the oxichloride $SbCl_3O$; and with sulphuretted hydrogen, to produce a crystalline mass of the sulphochloride $SbCl_3S$. Its decomposition by excess of water to furnish a white precipitate, at first of the unstable hydrate H_3SbO_4 or $Sb(HO)_3\acute{O}$, and eventually of antimonic acid $HSbO_3$ or $Sb(HO)\ddot{O}_2$.

Oxide, Sb_2O_5; made by gently heating antimonic acid:

$$2HSbO_3 = H_2O + Sb_2O_5$$

A yellowish-white powder, of sp. gr. 6·6, insoluble in water, convertible by ignition into the intermediate oxide Sb_2O_4.

Acid or hydrate, $HSbO_3$; produced as above, and by acting on metallic antimony with strong nitric acid containing a little hydrochloric acid. A soft yellowish-white powder, practically insoluble in water though imparting to it an acid reaction, inso-

luble in cold ammonia, soluble in caustic potash, and to some extent in strong hydrochloric acid.

Potassium antimoniate $KSbO_3$ or $K_2O.Sb_2O_5$, producible by fusing antimonic oxide with potassium carbonate, preferably mixed with a little nitre. Usually made by deflagrating metallic antimony with nitre. Fused mass washed with cold water, and residue then boiled with water for some time until more or less completely dissolved. Production, one vaporating the solution, of a syrupy hydrate $K_2O.Sb_2O_5.5Aq$, perfectly re-soluble in water. Formation, on further heating this product, of an inferior hydrate and eventually of the anhydrous salt, both insoluble in cold water, but dissolving almost completely on ebullition. Only a small residue left of the di-antimoniate $K_2O.2Sb_2O_5$; also producible, by passing a current of carbonic acid gas through the neutral antimoniate solution, as a white precipitate insoluble in water, but soluble in dilute potash to re-form the original salt.

Potassium parantimoniate made by evaporating down solution of the above antimoniate to syrupy consistency in a silver dish, with addition of solid caustic potash from time to time. After sufficient evaporation, contents of the dish resolved on cooling into a granular deposit of the neutral parantimoniate $K_4Sb_2O_7$ or $2K_2O.Sb_2O_5$, and a strongly alkaline mother-liquor. Drained deposit, washed with a little water, and thereby converted into the acid parantimoniate $K_2H_2Sb_2O_7$ or $2KHO.Sb_2O_5$ (Fremy's bimeta-antimoniate). Freshly made solution of this salt characterised by its giving, with sodium salt solutions, a white crystalline precipitate of sodium parantimoniate $Na_2H_2Sb_2O_7.6Aq$. But the solution speedily changed on keeping into one of ordinary potassium antimoniate, not precipitative of sodium salts.

Antimonious antimoniate, Sb_2O_4 or $Sb_2O_3.Sb_2O_5$; found native as cervantite, in massive state and in acicular crystals. Made by igniting antimonic oxide Sb_2O_5 ; or by roasting antimonious oxide Sb_2O_3; or by acting on powdered antimony with nitric acid, and heating the product. A yellowish-white powder, of sp. gr. 6·7, infusible and unchangeable in composition, but

becoming temporarily yellow, by heat. Compound regarded as an antimonylic antimoniate, or as an antimonious ox-antimoniate, tartar-emetic being the corresponding potassio-tartrate or oxi-tartrate:

$$HSbO_3 \qquad (SbO)'SbO_3 \qquad \overset{'''}{Sb}\begin{cases}\overset{''}{O}\\ SbO_3\end{cases}$$

$$HK\overset{''}{T} \qquad (SbO)'K\overset{''}{T} \qquad \overset{'''}{Sb}\begin{cases}\overset{''}{O}\\ K\overset{''}{T}\end{cases}$$

Its reaction with cream of tartar to form tartar-emetic and leave residue of antimonic acid:

$$(SbO)SbO_3 \quad + \quad HK\overset{=}{T} \quad = \quad HSbO_3 \quad + \quad (SbO)K\overset{''}{T}$$

Sulphide, Sb_2S_5; made by passing sulphuretted hydrogen through solution of antimonic chloride in aqueous tartaric acid; and by acidifying alkali sulphantimonite solutions. *An orange-yellow precipitate, decomposible by heat into antimonious sulphide and sulphur,* soluble in hydrochloric acid with formation of sulphuretted hydrogen and sulphur, and readily soluble in alkali hydrate and sulphide.

Alkali sulphantimoniates well-defined crystalline salts, producible as above, and in other ways. Sodium sulphantimoniate $Na_3SbS_4.9Aq$, known as Schlippe's salt, made by grinding up antimonious sulphide, sulphur, sodium carbonate, and quicklime into a paste with water. Paste digested with hot water, and filtrate evaporated. Deposition of the salt therefrom in large, transparent, slightly yellowish, tetrahedral crystals.

(81.) Bismuth.

A far from abundant element, occurring principally in the metallic state dispersed through a matrix of quartz; but also met with in form of oxide Bi_2O_3, as bismuth-ochre; of sulphide Bi_2S_3, as bismuthine; of telluro-sulphide $Bi_2(Te_2S)$, as tetradymite; and of sulpho-bismuthite in several more or less well-defined minerals.

Bismuth usually extracted from its matrix by heating the ore

in inclined iron tubes running across a furnace, and allowing the fused metal to flow out at lower ends of the tubes. Bismuth, being very easily reducible, obtainable on small scale and in pure state by heating a mixture of its basic nitrate and black flux.

A somewhat hard, feebly sonorous, brittle metal, highly lustrous, and of a characteristic reddish tinted white colour. Its sp. gr. 9·8. Its fusion at 264°, and solidification on cooling with considerable expansion. Its ebullition at a full white heat, and free vaporisation at inferior temperatures. Bismuth highly crystalline in texture. Cup of rhombohedral crystals approaching very closely to cubes, often beautifully iridescent, obtained by allowing fused metal to cool slowly, piercing solidified crust, and pouring away melted interior.

Bismuth permanent at ordinary temperatures, rapidly oxidisable at a red heat. Its easy attackability by chlorine, bromine, iodine, and sulphur. Its indifference to aqueous hydrochloric acid and sulphuric acids. Its solution in strong sulphuric acid at a gentle heat with formation of bismuth sulphate and sulphurous anhydride; and ready solution in not too dilute nitric acid with formation of bismuth nitrate and nitric oxide.

Rose's fusible metal an alloy of bismuth with tin and lead, in proportions $PbSn_2Bi_2$, becoming pasty and melting below 100°. Its anomalous contraction in solid state, when heated from 35° to 55°. Fusibility of most alloys promoted by presence of bismuth. Existence of cadmium-tin-lead-bismuth alloys fusible even at 60°. Introduction of bismuth into highly fusible solders; and its admixture with lead to form the alloy for permanent pencils.

Formation by bismuth of a well defined series of triad or bismuthous compounds, typified by bismuth chloride $BiCl_3$, oxide Bi_2O_3, &c.; and of a few less known pentad compounds typified by bismuthic oxide B_2O_5. Non-existence of any bismuth hydride BiH_3. Compound represented, however, not only by halogen but by hydrocarbon derivatives as bismuth chlorethide $BiEt_2Cl$, ethide $BiEt_3$, &c.

BISMUTHOUS COMPOUNDS.

Chloride, $BiCl_3$; made by passing chlorine gas over gently heated bismuth; or by distilling finely powdered bismuth with corrosive sublimate; or by evaporating down a hydrochloric acid solution of bismuth oxide, and distilling the residue.

An opaque greyish-white mass, readily fusible and volatile, deliquescent in moist air, and freely soluble in aqueous hydrochloric acid. Similar solution produced by dissolving bismuth oxide in hydrochloric acid. Combination of bismuth chloride with chloride of hydrogen, chloride of alkali-metal &c., to form crystallisable double salts. Dissolution of bismuth chloride in small quantity of water. Decomposition of the produced solution, and of solution of the chloride in not too great an excess of acid, by free addition of water, with precipitation of bismuth oxichloride $Bi\acute{O}Cl$, and liberation of hydrochloric acid holding some bismuth chloride in solution:

$$BiCl_3 \quad + \quad H_2O \quad = \quad Bi\acute{O}Cl \quad + \quad 2HCl$$

The oxichloride a white insoluble compound, fusing at a red heat without decomposition. Bismuth bromide $BiBr_3$, very similar to the chloride. The iodide BiI_3, thrown down from bismuth solutions by iodide of potassium as a brown crystalline precipitate. Decomposition of both compounds by excess of water, to furnish the oxybromide BiOBr, and oxy-iodide BiOI, respectively.

Oxide, Bi_2O_3; found native, though rarely, as bismuth-ochre. Made by igniting bismuth nitrate, carbonate, or hydrate; or by heating the metal itself in a current of, or with free exposure to, air. A dull yellow powder, of sp. gr. 8·2, becoming darker when heated, melting into a brown liquid, and solidifying on cooling into a crystalline mass. Its easy reduction by hydrogen, charcoal, &c.; and dissolution in most acids to form bismuth salts.

Bismuth oxide also obtainable, crystallised in yellow needles (orthorhombic prisms), by precipitating bismuth chloride or nitrate with excess of strong caustic alkali at a boiling heat.

Hydrate, $HBiO_2$ or $H_2O.Bi_2O_3$; a perfectly definite compound, produced as an amorphous white powder, on desiccation of the precipitate formed by adding bismuth nitrate to excess of dilute potash or ammonia. Precipitate changed into the crystalline oxide by ebullition with strong potash. An unstable sodium bismuthite $NaBiO_2$, corresponding to the hydrate, producible by fusing bismuth oxide with sodium carbonate.

Sulphide, Bi_2S_3; found native, though somewhat rarely, as bismuth glance, in amorphous state and crystallised isomorphously with stibnite in orthorhombic prisms. Its metallic lustre, bluish-grey colour, and sp. gr. 6·4. Compound producible, though with difficulty, by fusing bismuth with excess of sulphur; and in hydrated state, as a brown-black precipitate, by passing sulphuretted hydrogen through bismuth solutions. Bismuth sulphide less fusible than the metal. Its evolution of free sulphur at temperatures but little above its melting point; and ready oxidation when heated in air. Its solubility in hydrochloric acid with evolution of sulphuretted hydrogen; and insolubility in alkali hydrate, sulphide, and sulphydrate.

Alkali sulpho-bismuthites unknown. A few heavy-metal sulpho-bismuthites found native, as tannenite $C\acute{u}BiS_2$, wittichenite $C\acute{u}_3BiS_3$, kobellite $Pb_3(BiS_3)_2$, &c. A sulpho-telluride of bismuth Bi_2Te_2S, analogous to bismuth glance, found native as tetradymite.

Subsulphide, or disulphide, Bi_2S_2 or BiS; the analogue of realgar, produced by fusing bismuth sulphide with metallic bismuth. Its separation on cooling, from excess of metal, in acicular orthorhombic prisms. Its high metallic lustre, greyish-white colour, and sp. gr. 7·3. Its non-evolution of sulphur, howsoever strongly heated in close vessels. Same compound obtainable as a radiated crystalline mass, by fusing bismuth with sulphur; and not unfrequently formed in process for making the trisulphide, notwithstanding presence of sulphur in excess.

A suboxide of bismuth, analogous to the above sulphide, producible by oxidising bismuth in current of air at a temperature

below its melting point; and also by precipitating bismuthous chloride, in admixture with stannous chloride, by excess of potash. A grey crystalline powder, oxidisable and even combustible in air to furnish bismuthous oxide.

Salts. Existence of two classes of bismuthous salts, a class of normal salts typified by the chloride, nitrate, and sulphate; and a class of basic or oxysalts typified by the oxichloride, oxinitrate, and oxisulphate:

$$BiCl_3 \qquad Bi(NO_3)_3 \qquad Bi_2(SO_4)_3$$

$$Bi\begin{cases}\overset{\prime\prime}{O}\\ Cl\end{cases} \qquad Bi\begin{cases}\overset{\prime\prime}{O}\\ NO_3\end{cases} \qquad Bi_2\begin{cases}\overset{\prime\prime}{O}_2\\ \overset{\prime\prime}{SO}_4\end{cases}$$

These last frequently represented as salts of the monad radical bismuthyl, BiO:

$$(BiO)Cl \qquad (BiO)NO_3 \qquad (BiO)_2SO_4$$

Soluble normal salts made by dissolving the metal, or its oxide or sulphide, in acids. The corresponding basic salts insoluble or nearly so, and produced by action of water on the normal salts. Insoluble salts, both normal as the phosphate, and basic as the carbonate, alike precipitable by double decomposition.

Nitrate, $Bi(NO_3)_3$; or, with water of crystallisation, $2Bi(NO_3)_3.9Aq$. Made by dissolving bismuth in warm dilute nitric acid, evaporating liquid, and setting it aside to crystallise. Deposition of salt in large transparent anorthic prisms, soluble in dilute nitric acid, but decomposible by water. Its partial loss of nitric acid below 100°, conversion into half-hydrated basic salt $2(BiO)NO_3.Aq$ at 150°, and into bismuth oxide below 300°. The hydrated basic nitrate $(BiO)NO_3.Aq$, produced as an insoluble, amorphous, opaque white precipitate, by pouring nitric acid solution of bismuth nitrate into forty or fifty times its volume of water. Partial removal of nitric acid from the precipitate by prolonged washing, to leave a more basic salt. Production also of a basic nitrate, in form of semi-transparent silky precipitate having the same ultimate composition as above product, on diluting nitric acid solution of bismuth nitrate with moderate quantity of

cold water. Fresh precipitate somewhat soluble in pure water to form a solution becoming turbid after some time, and depositing greater part of its salt in the amorphous state. Gradual change also of undissolved precipitate into the insoluble amorphous compound. Soluble compound possibly an orthonitrate, $(BiO)H_2NO_4$.

Carbonate, $(BiO)_2CO_3.Aq$; formed as an opaque white precipitate, by decomposing nitric acid solution of bismuth nitrate with excess of alkali carbonate.

Sulphate, $Bi_2(SO_4)_3$; made by heating metallic bismuth with strong sulphuric acid. A white amorphous mass, soluble in dilute sulphuric acid and obtainable on evaporation in acicular crystals. Basic sulphate $(BiO)_2SO_4$, made by sufficiently heating the normal salt, or by decomposing it with water and drying the product. An insoluble white powder, becoming temporarily yellow by heat.

Phosphate, $BiPO_4$; thrown down as an opaque white precipitate, on adding sodium phosphate to solution of bismuth nitrate in dilute nitric acid. Its fusion by heat, and solidification on cooling into an enamel-like mass.

BISMUTHIC COMPOUNDS.

Oxide, Bi_2O_5; a brown powder, made by heating bismuthic hydrate to 130°. Its decomposition, when further heated, into bismuthous oxide and oxygen. Its solution in hydrochloric acid with evolution of chlorine, and in sulphuric acid and nitric acid with evolution of oxygen.

Hydrate, $HBiO_3$ or $H_2O.Bi_2O_5$; made by boiling bismuthous hydrate in solution of caustic potash during brisk passage through it of chlorine gas. Bright red product washed with water, digested in dilute nitric acid to remove potash and unaltered bismuthous oxide or hydrate, again washed and dried at 100°. Compound soluble in heated aqueous potash. Deposition of salt $KHO.Bi_2O_5$ on neutralising, and of the original hydrate $H_2O.Bi_2O_5$ on acidifying, produced solution with nitric acid.

Existence of a little known bismuthous bismuthate Bi_2O_4, or $Bi_2O_3.Bi_2O_5$. Its decomposition by nitric acid to form bismuthous nitrate and bismuthic acid.

Solid bismuth compounds, heated with carbonate of sodium on charcoal before the blowpipe, reducible with formation of brittle metallic bead, and yellow incrustation.

Bismuthous solutions recognisable, either at once or after evaporation, by giving upon free dilution with water a white precipitate of basic salt, insoluble in tartaric acid and turned black by sulphuretted hydrogen. Also, by giving with sulphuretted hydrogen, either at once or after cautious dilution, a black precipitate of bismuthous sulphide, insoluble in sulphide of ammonium, soluble in hydrochloric acid to form a solution precipitable by water as above. Also, by giving with caustic and carbonated alkalis, white precipitates insoluble in excess of the precipitants.

(82.) VANADIUM.

Occurrence of vanadium, as a definite mineral, in form of the different rarely met with lead vanadiates, namely, the metavanadiate or dechenite PbV_2O_6; the paravanadiate or descloizite $Pb_2V_2O_7$; and the orthovanadiate-chloride or vanadite $Pb_3V_2O_8.\frac{1}{3}PbCl_2 = \frac{1}{2}Pb_5(VO_4)_3Cl$. Vanadium also found somewhat widely but very minutely distributed, as in many varieties of clay; and in certain iron ores, and metal and slag obtained therefrom. Discovery by Roscoe of presence of vanadium in some metalliferous triassic sandstones worked at Alderley Edge and Mottram St. Andrew's, in Cheshire. Existence of nearly 2 per cent. of vanadium in a lime precipitate obtained in working up cobalt ore from Mottram.

Vanadium extracted in first instance by roasting above lime precipitate with soda-ash. Crude sodium vanadiate dissolved out, and freed from arsenic &c. by treating the acidified solution with sulphuretted hydrogen. Or solution of lead vanadiate in nitric acid treated with sulphuretted hydrogen. In either case, resulting

blue filtrate of reduced hypovanadic salt precipitated by ammonia, and dried precipitate oxidised into vanadic oxide V_2O_5, by nitric acid. Crude oxide further purified by boiling it up in ammonium carbonate solution, and recrystallising the sparingly soluble ammonium vanadiate.

Formation by vanadium of four well-defined series of compounds (Roscoe). A pentad or vanadic series, exemplified by vanadic chloride or oxi-chloride $\overset{v}{V}OCl_3$, and vanadic oxide or anhydride V_2O_5; the latter compound reacting with both alkalis and acids to form soluble salts such as potassium vanadiate $K_2O.V_2O_5$ or KVO_3, and vanadic sulphate $V_2O_5.3SO_3$(?). A series of tetrad or hypovanadic compounds typified by hypovanadic chloride VCl_4, and hypovanadic oxide VO_2 or V_2O_4; the latter compound reacting less decidedly with alkalis and more decidedly with acids than vanadic oxide. A series of triad or vanadous compounds typified by vanadous chloride VCl_3, the oxide V_2O_3, and a characteristic nitride $\overset{'''}{V}N$. Lastly, a series of diad or hypovanadous compounds typified by hypovanadous chloride VCl_2, and the oxide VO or V_2O_2.

Vanadium obtainable in metallic state by action of absolutely dry and air-free hydrogen upon ignited hypovanadous chloride VCl_2. Process successful only with employment of elaborate precautions, rendered necessary by tendency of the chloride, and of reduced metal at a red heat, to become oxidised, and by impossibility of reducing oxivanadium compounds to metallic state, whether by hydrogen, carbon, or sodium. Light-grey metallic powder, lustrous under the microscope, of sp. gr. 5·5; unalterable by water and by moist or dry air; combustible in oxygen and air to state of vanadic oxide V_2O_5; spontaneously combustible in chlorine to form hypovanadic chloride VCl_4; and absorptive at a red heat of nitrogen to form vanadous nitride VN. Metal unattackable by hydrochloric and dilute sulphuric acid; slowly attackable by hydrofluoric and strong sulphuric acid; readily dissolved by nitric acid, strong or dilute, and converted by fused but not by aqueous alkali into alkali vanadiate.

VANADIC COMPOUNDS.

Oxichloride, $VOCl_3$; made by action of chlorine on heated hypovanadous oxide VO, or on mixture of higher oxide with charcoal. A golden yellow liquid, of sp. gr. 1·84, boiling at 127°, to furnish a red vapour of density $86 \cdot 8 = \frac{51 + 16 + 106 \cdot 5}{2}$. Its decomposition by water, in deficit to form hydrochloric acid and vanadic oxide, and in excess to furnish a solution of vanadic hydrochloride.

Oxide or anhydride, V_2O_5; made by heating vanadic sulphate, ammonium vanadiate, or any inferior vanadium oxide with access of air. The inferior oxides conveniently oxidisable also by means of nitric acid. A reddish yellow powder, sparingly soluble in water to form a yellow solution of slightly acid reaction. Its fusion by heat, and solidification on cooling into a red crystalline mass.

Solubility of vanadic oxide in acids to form red or yellow saline solutions, undergoing reduction when boiled. The sulphate solution crystallisable by spontaneous evaporation. The hydrochloride solution decomposed spontaneously, rapidly on ebullition, with evolution of chlorine and formation of blue hypovanadic hydrochloride. Yellow-red solution in acid of vanadic oxide reduced to blue hypovanadic solution by sulphydric, sulphurous, and oxalic acids; somewhat curiously to green vanadous solution by magnesium; and to pale lavender hypovanadous solution by zinc or sodium-amalgam.

Solubility of vanadic oxide in alkalis to form vanadiates. Formation, by decomposing alkali vanadiate solution with nitric acid, of vanadic acid or hydrate $H_2O.V_2O_5$ or HVO_3. A bulky flocculent precipitate, drying up over oil of vitriol into a brown red powder. Similar precipitate formed by neutralising acid solutions of vanadic oxide.

Combination of vanadic oxide or anhydride with bases to form definite salts. Occurrence of vanadiates referrible to phosphate and paraphosphate types, as cupric vanadiate $3CuO.V_2O_5$ or

$Cu_3(VO_4)_2$, and descloizite $2PbO.V_2O_5$ or $Pb_2\left\{\begin{matrix}VO_4\\VO_3\end{matrix}\right.$. Isomorphism of vanadite $Pb_5(VO_4)_3Cl$, with pyromorphite $Pb_5(PO_4)Cl$, and replacement in former mineral of variable amount of vanadium by phosphorus. Liberation from fused sodium carbonate of three molecules of carbonic by one of vanadic anhydride:

$$3(Na_2O.CO_2) + V_2O_5 = 3Na_2O.V_2O_5 + 3CO_2$$

or

$$3Na_2CO_3 + V_2O_5 = 2Na_3VO_4 + 3CO_2$$

Majority of artificial vanadiates, however, referrible to the nitrate or metaphosphate type, as sodium vanadiate $Na_2O.V_2O_5$, or $NaVO_3$, corresponding to native mineral dechenite $P\overset{''}{b}O.V_2O_5$ or $P\overset{''}{b}(VO_3)_2$. Existence also of stylous or anhydro-vanadiates referrible to types $M_2O.2V_2O_5$ or $M_2V_4O_{11}$, and $M_2O.3V_2O_5$ or $M_2V_6O_{16}$.

Normal vanadiates for the most part white or pale yellow; the anhydro-salts orange-red. Hence development of red colour on acidifying normal vanadiate solutions. Ammonium di-vanadiate $(NH_4)_2O.2V_2O_5.4Aq$, formed in large orange-red crystals by saturating warm aqueous ammonia with vanadic oxide, and leaving liquid to evaporate. The metavanadiate $(NH_4)_2O.V_2O_5$ or NH_4VO_3, obtained by adding excess of ammonia to solution of above salt, and suspending a lump of sal-ammoniac in the liquid. Colourless transparent crystalline crusts, soluble in boiling water, sparingly soluble in cold water, almost insoluble in sal-ammoniac solution. Existence of similar, stylous and normal, sodium and potassium compounds. The normal salts less soluble in caustic alkali than in water. Their aqueous solutions decomposed by solid sal-ammoniac with precipitation of ammonium vanadiate.

HYPOVANADIC COMPOUNDS.

Chloride, VCl_4; made by passing chlorine over heated vanadous nitride; or a mixture of chlorine and vanadic oxichloride over ignited charcoal in large excess. A dark, reddish-brown, fuming liquid, of sp. gr. 1·83, boiling point 154°, and vapour-density $96{\cdot}5 = \frac{51 + 142}{2}$. Hypovanadic chloride unaffected by

chlorine at any temperature. Its gradual decomposition, by ebullition or exposure to light, into vanadous chloride and free chlorine. Its dissolution in water to form blue solution of hypovanadic hydrochloride. Existence of a hypovanadic oxichloride $VOCl_2$, producible by reducing vanadic oxichloride $VOCl_3$, with metallic zinc.

Oxide, VO_2 or V_2O_4; produced in anhydrous state, by exposure of vanadous oxide to air at ordinary temperatures, as a blue crystalline solid, easily oxidisable into orange vanadic oxide, and dissolving in acids to form hypovanadic salts, some of them crystallisable. The hydrochloric solution also made by action of water on hypovanadic chloride; by ebullition of, or action of reducing agents on, hydrochloric solution of vanadic oxide; and by oxidising action of current of air upon hydrochloric solution of inferior oxides. Grey hypovanadic hydrate thrown down from solution of hypovanadic salts by caustic or carbonated alkali. Precipitate at first insoluble in water, but after exposure to air soluble, forming a greenish hypovanadic-vanadic solution. Precipitate soluble in moderate excess of precipitant. Resulting alkali hypovanadiate insoluble in, and precipitable by large excess of, alkali.

Sulphide, VS_2 or V_2S_4; produced in hydrated state, as a black or brown precipitate, by adding a hypovanadic solution to excess of alkali mono-sulphide, and acidifying. Compound resoluble in alkali mono-sulphide to form a purple sulphypovanadiate solution.

VANADOUS COMPOUNDS.

Chloride, VCl_3; best made by continued ebullition of hypovanadic chloride, and desiccation of the solid product at 160°, in current of carbanhydride. Shining puce-coloured scales, of sp. gr. 3·0, not volatilisable; decomposible when heated in air, to yield vanadic oxide and oxichloride; and when heated in hydrogen, to yield in succession hypovanadous chloride and metallic vanadium. Hygroscopicity and solubility in water of vanadous chloride to form a brown solution, changing to bright

green on acidification. Similar green solution produced by reducing hydrochloric solution of vanadic or hypovanadic oxide by metallic magnesium. Also by cautious oxidation of hydrochloric solution of hypovanadous oxide. Existence of a vanadous oxichloride $V\ddot{O}Cl$, producible as a brown powder by reaction of vanadic oxichloride and hydrogen at a red heat.

Oxide, V_2O_3; made by igniting vanadic oxide in current of hydrogen gas. A black, infusible, lustrous powder, slowly oxidisable into hypovanadic oxide on mere exposure, combustible into vanadic oxide at a moderate heat, and reactive with chlorine to produce vanadic oxide and oxichloride:

$$3V_2O_3 \quad + \quad Cl_{12} \quad = \quad V_2O_5 \quad + \quad 4VOCl_3$$

Nitride, VN; producible by reaction of vanadic oxichloride with ammonia, and in other ways. Best made by prolonged strong ignition of ammonium vanadiate, or of vanadic or vanadous oxide, in current of ammonia. A greyish powder, permanent in the air, formerly mistaken for metallic vanadium. Its attackability at a red heat by chlorine to furnish hypovanadic chloride.

HYPOVANADOUS COMPOUNDS.

Chloride, VCl_2; produced in loose, micaceous, apple-green hexagonal scales, of sp. gr. 3·2, by passing vaporised hypovanadic chloride, with excess of hydrogen, through glass tube heated to dull redness. Compound reducible by hydrogen at a bright red heat to leave metallic vanadium; non-volatilisable, either alone or in current of carbanhydride or hydrogen. Its rapid deliquescence in air; but its dissolution in water, save when previously deliquesced, not instantaneous, the scales floating about for some time. Eventual production of lavender liquid, identical in tint with that obtainable by reducing sulphuric acid solution of vanadic oxide with zinc or sodium-amalgam. Either solution extremely oxidisable; its change of colour on exposure to air, from pale lavender to chocolate brown, being equally rapid with the browning of alkaline pyrogallates. By continued

passage of air through it, the acidified lavender solution rendered green and finally deep blue. Equally rapid bleaching of indigo, by its reduction with hypovanadous chloride, as by its oxidation with free chlorine.

Oxide, VO or V_2O_2; made by subjecting vaporised vanadic oxichloride, $VOCl_3$, mixed with excess of hydrogen, to strong ignition. A lustrous, grey, crystalline powder or crust, of sp. gr. 3·64. Product difficultly fusible in close vessels, combustible in air, and insoluble in acids, except the nitro-muriatic.

(83.) Niobium and Tantalum.

Niobium or columbium found chiefly as ferrous niobiate in the columbite of Massachusetts and Bavaria; also in samarskite, a complex yttrium urano-niobiate; and as a minor constituent of other minerals.

Tantalum found chiefly as ferrous tantalate in the tantalite of Sweden, Finland, and Greenland. Also as yttrium tantalate; and as a minor constituent of numerous complex minerals. Presence of some tantalum in most columbites, and of some niobium in most tantalites.

Columbite discovered by Hatchett in 1802; tantalite by Ekeberg in 1803. Minerals pronounced identical by Wollaston in 1807; differentiated by Rose in 1846; further studied, and formulæ of the respective chlorides and oxides as penta-compounds established by Marignac in 1866, chiefly on basis of Deville and Troost's determination of vapour-densities of the chlorides. Tantalic anhydride previously represented by formula TaO_2 or TaO_3, analogous to TiO_2 and WO_3 respectively, instead of by Ta_2O_5, analogous to P_2O_5.

Niobium and tantalum obtained by heating potassium fluoniobiate and fluo-tantalate respectively with sodium:

$$2(K_2F_4.TaF_5) + Na_{10} = 4KF + 10NaF + Ta_2$$

Black powders, oxidising and becoming incandescent when gently heated in air, scarcely attacked by ordinary acids, soluble in

hydrofluoric acid with evolution of hydrogen, and readily soluble in nitro-hydrofluoric acid. Their conversion into potassium niobiate and tantalate respectively by fusion with caustic potash, and into the two anhydrides by fusion with acid sulphate of potassium.

Fluorides; made in solution by dissolving niobic and tantalic hydrates in aqueous hydrofluoric acid. Residues of niobic oxifluoride $Nb\ddot{O}F_3$, and tantalic oxifluoride $Ta\acute{O}F_3$, left on evaporating the solutions. Formation, on adding potassium fluoride to above niobic solution, of an easily soluble crystallisable hydrated oxifluo-niobiate $2KF.NbOF_3$. Conversion of salt into the fluoniobiate $2KF.NbF_5$ by its crystallisation from aqueous hydrofluoric acid. Solution of neither salt precipitated by ebullition.

Formation, on adding potassium fluoride to above tantalic fluoride solution, of potassium fluo-tantalate $2KF.TaF_5$, as a sparingly soluble crystalline salt. Its solution decomposed by continuous boiling, with precipitation of an acid oxifluo-tantalate $KF.TaOF_3$. Reaction distinctive between tantalum and niobium, and available for their separation from each other.

Chlorides; made by passing chlorine gas over ignited mixtures of the respective oxides with charcoal. Niobic chloride $NbCl_5$, a yellow, easily fusible, volatile solid, of vapour-density $135{\cdot}75 = \frac{94 + 5(35{\cdot}5)}{2}$. Formation simultaneously with above compound of a white, infusible, not so volatile oxichloride $NbCl_3O$, of vapour-density $109{\cdot}25 = \frac{94 + 16 + 3(35{\cdot}5)}{2}$. Both compounds decomposible by water with formation of hydrated niobic oxide. Tantalic chloride $TaCl_5$, a yellow sublimate, melting at 221°, volatilising below its melting point, and only partially decomposing by continued ebullition with water to furnish a precipitate of hydrated tantalic oxide. Its vapour density $179{\cdot}75 = \frac{182 + 5(35{\cdot}5)}{2}$.

Oxides; obtained from columbite and tantalite by igniting the minerals with caustic potash, dissolving respective fused products in water, and acidifying solutions; or by fusing the minerals with acid sulphate of potassium, digesting products with water, and boiling the residues with strong hydrochloric acid.

Compounds obtained by former process as amorphous hydrates; by latter process as crystalline oxides. Hydrated niobic oxide also obtained by decomposing the chloride or oxichloride with water. Its solubility in hydrochloric acid, though with much difficulty, and in aqueous alkali. The anhydrous oxide, an amorphous or crystalline white powder, of sp. gr. 4·5, insoluble in acids save the hydrofluoric, and attackable by fused but scarcely by aqueous caustic alkali.

Occurrence of precipitated tantalic oxide as a snow-white bulky hydrate, readily soluble in hydrochloric acid, and in aqueous alkali. The anhydrous oxide an amorphous or crystalline white powder, of sp. gr. 8·0, insoluble save in hydrofluoric acid, and attackable by caustic alkali only when in state of fusion. Oxides and hydrates of both metals unaffected by sulphide of ammonium.

Niobiate of iron $FeO.Nb_2O_5$, and tantalates of iron and yttrium, $FeO.Ta_2O_5$ and $YO.Ta_2O_5$, found native as the minerals columbite, tantalite, and yttro-tantalite. Alkali-salts, obtainable by fusion of the respective oxides with caustic alkali, soluble, crystallisable compounds, of complex and varied constitution. Most common potassium salts represented by formulæ $4K_2O.3Nb_2O_5$ and $4K_2O.3Ta_2O_5$ respectively.

Tantalic oxide apparently more basylous than the niobic. Its formation of a sulphate, in addition to its ready formation of a hydrochloride. Existence in case of tantalum of an inferior oxide, apparently Ta_2O_4, obtained, by strongly igniting the pentoxide in charcoal-lined crucible, as a hard dark-grey mass, and reconverted into the pentoxide when gently heated in air. The solution of tantalic oxide in sulphuric acid reduced by metallic zinc, with production of deep blue colour.

CHAPTER X.

(84.) Chromium Elements.

Chromium—Molybdenum, Tungsten.

Difficultly fusible metals, associated with one another by common property of forming volatile hexad oxichlorides, $CrCl_2O_2$, $MoCl_2O_2$, and WCl_2O_2, and the corresponding oxides CrO_3, MoO_3, and WO_3, the latter combining with bases to form stable well-defined salts analogous to, and in some instances isomorphous with, the corresponding sulphates $\overset{''}{M}O.SO_3$ or $\overset{''}{M}SO_4$. Chromium as a hexad, markedly comparable with vanadium as a pentad element; but molybdenum and tungsten not comparable in the same way with niobium and tantalum respectively, or very intimately related to each other. Symbols and atomic weights:

	Hexad.			Pentad.	
Cr	Chromium	52·5	V	Vanadium	51
Mo	Molybdenum	92	Nb	Niobium	94
W	Tungsten	184	Ta	Tantalum	182

Association of chromium and the other two hexad metals not well marked, limited to their respective series of hexad compounds; and, even in these series, not extending to a parallelism of sulphides. Formation by molybdenum and tungsten of the trisulphides, MoS_3 and WS_3, both combining as sulphanhydrides with alkali-metal sulphides, to form characteristic sulpho-salts. Non-existence of any such chromium sulphur compounds.

Formation also, by molybdenum and tungsten, of well-defined, metal-like, crystalline di-sulphides, MoS_2 and WS_2, corresponding to the volatile tetrachlorides, $MoCl_4$ and WCl_4 respectively.

Formation by chromium of a mixed oxide $Cr_2O_3.CrO_3$ or $3CrO_2$, but not of any real tetrad compound.

Formation by chromium of a sesquioxide Cr_2O_3, sesquichloride Cr_2Cl_6 or $CrCl_3$, and a series of sesqui-salts, similar in constitution and properties to alumina Al_2O_3, aluminic chloride Al_2Cl_6 or $AlCl_3$, and ordinary aluminic salts. These compounds without any molybdenum and tungsten analogues.

Further formation by chromium and molybdenum, but not by tungsten, of an unstable series of diad compounds referrible to the types $\overset{''}{M}O$ and $\overset{''}{M}Cl_2$ &c.

(85.) Chromium.

Its principal source, chrome-iron-stone $FeCr_2O_4$. Its occurrence also as chrome-ochre Cr_2O_3, and as crocoisite $PbCrO_4$. Its existence as a minor constituent of many iron ores, of meteoric irons, and of certain green or red minerals, as emerald, greenserpentine, and pyrope.

Metallic chromium but little known. Its production as a greyish-white, extremely hard, infusible mass, by subjecting mixed chromic oxide and charcoal to the heat of a blast furnace. Or chromic chloride, in admixture with the chlorides of potassium and sodium, packed in a crucible, covered with excess of metallic zinc, and heated to redness (Wöhler). Button of zinc containing chromium thereby obtained. Zinc dissolved away by dilute nitric acid, and chromium left as a greenish-grey, glistening, crystalline powder, with here and there whiter and larger crystals, apparently quadratic octahedrons, of sp. gr. 6·8. Chromium, in this form, slowly and imperfectly oxidisable in current of heated air or steam, but combustible in a current of oxygen, attacked by chlorine with incandescence, readily oxidised by fused nitre, unaffected by nitric acid strong or dilute, soluble in hydrochloric acid as chromous chloride with evolution of hydrogen, and also in dilute sulphuric with aid of a gentle heat to start the reaction.

Formation by chromium of three definite series of compounds,

namely, an unimportant diad or chromous series, typified by chromous chloride $CrCl_2$; a triad or quasi-triad or chromic series, typified by chromic chloride $CrCl_3$ or Cr_2Cl_6, and chromic oxide Cr_2O_3; and a hexad or chromate series, typified by chromate fluoride CrF_6, oxichloride CrO_2Cl_2, and anhydride CrO_3. Existence also of a few intermediate compounds, and of an unstable perchromate oxide or hydrate.

CHROMATE COMPOUNDS.

Fluoride, CrF_6; made by distilling some chromate salt, usually chromate of lead, with fluor-spar and oil of vitriol, in a leaden or platinum retort:

$$3CaF_2 + PbCrO_4 + 4H_2SO_4 = CrF_6 + PbSO_4 + 3CaSO_4 + 4H_2O$$

An orange-red vapour condensable into a blood-red liquid, boiling almost at ordinary temperature, fuming freely in moist air with production of hydrofluoric acid and chromate anhydride, and reacting violently with water to yield the same products:

$$CrF_6 + 3H_2O = CrO_3 + 6HF$$

Oxichloride, CrO_2Cl_2; made by distilling a mixture of sodium chloride and potassium chromate (preferably fused together) with oil of vitriol in excess:

$$2NaCl + K_2CrO_4 + 4H_2SO_4 = CrO_2Cl_2 + 2NaHSO_4 + 2KHSO_4 + 4H_2O$$

A heavy, fuming, orange-brown, almost black liquid, of sp. gr. 1·71, boiling point 118°, and vapour-density $77·5 = \frac{52 + 32 + 71}{2}$. Its decomposition by water or moisture with formation of hydrochloric acid and chromate anhydride:

$$CrO_2Cl_2 + H_2O = CrO_3 + 2HCl$$

Non-producibility of any corresponding bromine or iodine compound; whence capability of effecting volatilisation of a chromate, from mixture of a chromate salt with oil of vitriol,

distinctive between a chloride and a bromide or iodide. Action of chromate oxichloride, especially upon organic substances, as a violent oxidising and frequently inflaming agent. Decomposition of vaporised compound by its passage through ignited porcelain tube, with formation of crystalline chromic oxide:

$$2CrO_2Cl_2 = Cr_2O_3 + O + Cl_4$$

Oxide, or anhydride, CrO_3. Crude potassium chromate $K_2O.CrO_3$ or K_2CrO_4, made in first instance by roasting, in current of air, a mixture of chrome-iron-ore and potassium carbonate together with some chalk to promote oxidation by preventing fusion of the mass:

$$2(FeO.Cr_2O_3) + O_7 + 4(K_2O.CO_2) = Fe_2O_3 + 4(K_2O.CrO_3) + 4CO_2$$
$$\text{or } 2FeCr_2O_4 + O_7 + 4K_2CO_3 = Fe_2O_3 + 4K_2CrO_4 + 4CO_2$$

Resulting potassium chromate extracted with water, solution acidified with nitric acid, and so-produced potassium dichromate crystallised out:

$$\left.\begin{array}{l}2K_2CrO_4 \text{ or} \\ 2(K_2O.CrO_3)\end{array}\right\} + 2HNO_3 = \left.\begin{array}{l}K_2Cr_2O_7 \text{ or} \\ K_2O.2CrO_3\end{array}\right\} + 2KNO_3 + H_2O$$

Saturated solution of potassium dichromate mixed with rather more than its own bulk of oil of vitriol and set aside. Considerable separation on cooling (through its sparing solubility in sulphuric acid of resulting strength) of chromate anhydride, in form of crimson needles. Crystals drained on a tile; and, if requisite, purified by solution in water and recrystallisation, preferably after precipitation of sulphuric acid by exact sufficiency of barium dichromate solution.

Or chromate fluoride vapour conveyed into platinum crucible lined with wet filtering paper.

Occurrence of chromate anhydride in crimson-red needles, or loose woolly masses, deliquescent and very soluble in water, forming an orange-red solution. Its temporary darkening by heat, fusion at 190°, and decomposition at 250° and upwards, eventually into chromic oxide and oxygen. Its decompositions,

when heated with sulphuric acid and hydrochloric acid, to evolve oxygen and chlorine respectively:

$$3H_2SO_4 + 2CrO_3 = Cr_2(SO_4)_3 + 3H_2O + O_3$$
$$12HCl + 2CrO_3 = Cr_2Cl_6 + 6H_2O + Cl_6$$

Its violent action as an oxidising agent upon alcohol, ammonia, &c., frequently attended with combustion or incandescence. Similar but quiet oxidising action of its aqueous solution, especially in presence of sulphuric or hydrochloric acid and at a gentle heat. For example, its ready oxidation of, and correlative reduction to the state of a chromic salt by, zinc, sulphuretted hydrogen, sulphurous acid, oxalic acid, alcohol, &c.

Non-existence of any definite chromate of hydrogen H_2CrO_4. But solution of the anhydride in water possessed of marked acid character, shown by its effervescing with carbonates &c. Recrystallisation of chromate anhydride, however, upon evaporation of the solution. Combination of the anhydride with bases to form neutral salts, such as K_2CrO_4, $PbCrO_4$, &c. Existence also of many basic or oxichromates, as di-plumbous oxichromate $PbO.PbCrO_4$ or Pb_2CrO_5. Non-existence of any acid or hydrogen chromate, such as *$KHCrO_4$*, corresponding to $KHSO_4$. Effect of acidifying the solution of a neutral chromate to produce a di- or anhydro-chromate as $K_2CrO_4.CrO_3$ or $K_2Cr_2O_7$. Producibility also of a potassic tri-chromate $K_2CrO_4.2CrO_3$ or $K_2Cr_3O_{10}$, by crystallising solution of the di-chromate in ordinary nitric acid. Combination also of chromate anhydride with alkali chlorides, as of potassium, to form the chloro-chromate $KCl.CrO_3$ or $KCrO_3Cl$, a compound intermediate between the oxichloride and the neutral salt:

$$Cl_2.CrO_2 \quad \text{or} \quad CrO_2Cl_2$$
$$\left.\begin{matrix}Cl\\KO\end{matrix}\right\}CrO_2 \quad ,, \quad KCrO_3Cl$$
$$(KO)_2CrO_2 \quad ,, \quad K_2CrO_4$$

Salt produced in orange needles, by dissolving potassium dichro-

mate in slightly diluted hydrochloric acid at a gentle heat, and setting aside:

$$K_2Cr_2O_7 + 2HCl = 2KCrO_3Cl + H_2O$$

Red potassium dichromate formed by acidifying solution of the neutral or yellow chromate; produced on manufacturing scale as above described, and purified by recrystallisation. Its occurrence in large, transparent, orange-red, four-sided prisms, melting below a red heat and solidifying unchanged as a crystalline mass. Its decomposition at a white heat, into the neutral chromate, chromic oxide, and oxygen:

$$2K_2Cr_2O_7 = 2K_2CrO_4 + Cr_2O_3 + O_3$$

Its deflagration with charcoal, sulphur, &c. Its solubility in 10 parts of water at 15°, and free solubility in boiling water. Its reaction with sulphuric, nitric, and hydrochloric acids to produce chromate anhydride, potassium trichromate, and potassium chlorochromate respectively. Its reactions with heated sulphuric and hydrochloric acids, similar to those of the anhydride, to evolve oxygen and chlorine respectively:

$$4H_2SO_4 + K_2Cr_2O_7 = 2K\overset{''}{Cr}(SO_4)_2 + 4H_2O + O_3$$

Frequent employment of mixed sulphuric acid and potassium dichromate to effect the oxidation of organic substances. Reduction of acidified solution of potassium dichromate, as of the anhydride, by sulphurous acid or anhydride, oxalic acid, &c. &c.:

$$H_2SO_4 + 3SO_2 + K_2Cr_2O_7 = 2K\overset{''}{Cr}(SO_4)_2 + H_2O$$

Partial reduction of potassium dichromate by paper, gelatine, &c. under exposure to sunlight, made the basis of different photographic processes.

Potassium chromate K_2CrO_4, usually made in solution, from the dichromate, by addition of caustic alkali. Production, on evaporation, of lemon-yellow pyramidal crystals, isomorphous with those of potassium sulphate. Free solubility of the salt in cold, and its yet greater solubility in boiling water. Solutions, whether

strong or exceedingly dilute, of a pale yellow colour. Salt recrystallisable only in presence of excess of alkali. Otherwise, deposition at first of the red dichromate, and afterwards from alkaline mother-liquor, of yellow chromate crystals. Production of dichromate by acidifying the yellow chromate solution, even with carbonic acid. The yellow chromate fusible but undecomposible by heat. Its decomposition, both in wet and dry way, by most reducing agents.

Sodium and ammonium chromates similar to those of potassium. Ammonium dichromate made by adding one part of chromate anhydride to a second part previously neutralised with ammonia, and evaporating. Decomposition of the salt by heat, with great intumescence, to yield chromic oxide:

$$(NH_4)_2Cr_2O_7 \quad = \quad N_2 \quad + \quad 4H_2O \quad + \quad Cr_2O_3$$

Similar decomposition of mixed potassium dichromate and salammoniac. Silver chromate Ag_2CrO_4, a dark red precipitate, producible in flocculent and crystalline states. Magnesium chromate $MgCrO_4.7Aq$, yellow, soluble, and isomorphous with Epsom salt. Barium chromate $BaCrO_4$, a yellow precipitate, insoluble in water and dilute acetic acid. The calcium and strontium salts somewhat soluble in water, readily in dilute acetic acid. Lead chromate $PbCrO_4$, found native as crocoisite in transparent yellow prismatic crystals. Produced as an orange-yellow precipitate, by decomposing a lead salt, in dilute solution, with chromate or dichromate of potassium. Fusion of the compound at a moderate heat and its solidification, on cooling, into a hard red-brown crystalline mass. Its decomposition, with evolution of oxygen, at a higher temperature, and ready reduction by organic substances heated with it. Hence employment of fused lead chromate in combustion-analysis of organic substances. Unfused lead chromate used as a pigment, under the name of chrome yellow. Its cheap production by acting on lead sulphate with potassium chromate solution. In calico printing, patterns printed with lead salt, and fabric passed through bath of chromate solution. Existence of a bright scarlet or orange basic lead chromate $Pb_2\left\{\begin{matrix}O\\CrO_4\end{matrix}\right.$,

used also as a pigment under the name of chrome red. Its production in very many ways, as by precipitating a basic lead salt with neutral alkali chromate; precipitating a neutral lead salt with mixed alkali chromate and hydrate; treating neutral lead chromate with caustic alkali, or boiling it with neutral potassium chromate, &c.

$$2PbCrO_4 + K_2CrO_4 = Pb_2\left\{\begin{matrix}O\\CrO_4\end{matrix}\right. + K_2Cr_2O_7$$

Compound produced of the finest colour by fusing neutral lead chromate with excess of nitre. In calico-printing, fabrics first printed or dyed with the neutral chromate, and then passed through boiling milk of lime.

Production, by reaction of peroxide of hydrogen (or hydrochloric acid solution of peroxide of barium) and an acidified solution of chromate anhydride or alkali chromate, of a temporary bright blue colour, quickly disappearing with effervescence of oxygen, and formation of a green chromic solution. Unstable blue compound known as perchromic acid, considered to be the analogue of permanganic acid and to have the formula $HCrO_4$ or $H_2O.Cr_2O_7$. With excess of hydrogen peroxide, two molecules of oxygen liberated for each molecule of chromic oxide produced:

$$H_2O_2 + 2CrO_3 = H_2O.Cr_2O_7 = H_2O.Cr_2O_3 + 2O_2$$

Solubility of perchromic acid in ether, to form a tolerably stable deep blue liquid; whence reaction leading to its production best effected in presence of ether. Blueing of ether by addition of acidified chromate solution habitually employed as a test for hydrogen peroxide. Immediate decomposition of perchromic acid, even when in ethereal solution, by addition of potash or soda.

Chromate solutions recognisable by their yellow or orange colour; by their furnishing with lead acetate solution a bright yellow precipitate of lead chromate; by their forming a blue compound with hydrochloric acid, peroxide of hydrogen and ether; and by their reduction, preferably after acidification with

hydrochloric or sulphuric acid, by addition to them of alcohol, stannous chloride, sulphurous acid, sulphuretted hydrogen, &c., the resultant green chromic solutions being mixed, in case of sulphuretted hydrogen reaction, with yellowish-white precipitate of sulphur.

CHROMIC COMPOUNDS.

Chloride, $CrCl_3$ or Cr_2Cl_6. Existence of chromic chloride in three distinct forms, namely an anhydrous violet insoluble crystalline form, a violet soluble crystallisable form, and a green soluble uncrystallisable form. Corresponding varieties of chromic sulphate and other chromic salts also met with.

The anhydrous chloride produced, as a micaceous puce-coloured sublimate, by passing chlorine gas over an ignited mixture of chromic oxide and charcoal. Compound quite unaffected by cold water, and purifiable by washing therewith. Its slow dissolution by prolonged boiling with water, in form of a green uncrystallisable liquid. Its ready solution also in cold water in presence of even a trace of chromous chloride, with formation of same green uncrystallisable liquid. Anhydrous chromic chloride scarcely affected by liquid reagents, including strongest acids and alkalis. Its reduction, by hydrogen at red heat, to state of chromous chloride and partly to that of metallic chromium. Its decomposition, when heated in current of air, with evolution of chlorine and formation of chromic oxide. Its ready oxidation by fused nitre and alkali carbonate.

Soluble violet chloride produced, by gently heating the green chloride in a current of hydrochloric acid or chlorine, in form of deliquescent scales, yielding a violet solution with water. Similar solutions made by decomposing the violet sulphate with chloride of barium, precipitating chrome alum with ammonia and dissolving the precipitate in hydrochloric acid, &c. Chlorine of violet solution completely precipitated by nitrate of silver.

The green chloride produced from above violet solution by simple ebullition, and from the anhydrous chloride by its prolonged ebullition with water, or rapidly in presence of a little

chromous or stannous chloride. Compound usually made by dissolving chromic oxide or hydrate in hydrochloric acid; or by reducing any chromate by ebullition with hydrochloric acid, either alone or preferably with a little alcohol to suffer oxidation (*vide* chromates). Production, by evaporating solution, of a non-crystalline dark green syrup, capable of being dried up into a green mass by current of heated air. The chlorine of green chromic chloride only partially precipitated by nitrate of silver, save upon heating therewith or after long standing.

Hydrates. Precipitation by ammonia from violet chromic solutions of a bluish-grey hydrate, soluble in excess of the precipitant, and soluble in acids with reproduction of violet solutions. Precipitation by ammonia from green chromic solutions of a dull green hydrate, less freely soluble in excess of the precipitant, soluble in acids with reproduction of green solutions. The precipitates thrown down by fixed alkali similarly characterised. Their free solubility in excess of cold fixed alkali, and complete reprecipitation on boiling the solution for some time, in form of a decidedly green hydrate. Obstinate retention of some fixed alkali by above precipitates. Solutions of chromic hydrate in excess of ammonia also precipitated on ebullition; and chromic salts, at a boiling heat, completely precipitated by excess of ammonia with formation of an alkali-free bluish-green hydrate $Cr_2O_3.7H_2O$ or $H_2Cr_2O_4.6Aq$, dissolving in acids with production of green solutions.

A chromic hydrate $Cr_2O_3.2H_2O$, insoluble in acids and alkalis, produced as a fine green pigment under the name of Guignet's green, by igniting mixture of potassium dichromate and boracic acid, decomposing produced chromic borate by ebullition with water, and removing last traces of boracic acid from resulting hydrate by its ebullition with alkali.

Oxide, Cr_2O_3; obtained, by gently heating the precipitated hydrate to below redness, as a dull green powder dissolving readily in acids to form green solutions. Action of a strong heat upon the oxide to effect its considerable shrinking and render it insoluble in acids. The amorphous insoluble oxide producible in many other ways,

as by igniting basic mercurous chromate $Hhg_2\left\{\begin{matrix}O\\CrO_4\end{matrix}\right.$, or ammonium dichromate $(NH_4)_2Cr_2O_7$, or potassium dichromate $K_2Cr_2O_7$ mixed with any combustible substance, as sulphur, lamp-black, starch, &c. Various technical processes employed for preparing the amorphous oxide of a fine green colour, for use as a pigment under the name of permanent green. Use of the oxide also for painting on porcelain, and for production of ornamental green glass and enamel. Chromic oxide irreducible by hydrogen, but reducible at an intense heat by charcoal. Its fusion in a forge-fire, and solidification into a black crystalline mass. Crystalline chromic oxide also formed by slowly passing chromate oxichloride vapour though a glass tube heated to dull redness, and in other ways. Greenish-black rhombohedral crystals, of sp. gr. 5·2, hard enough to scratch glass. Chromic oxide in any form convertible into soluble alkali chromate by its fusion with alkali carbonate and nitre.

Action of chromic oxide as a feeble anhydride to combine with bases, including chromous oxide; and as a stronger, though by no means powerful, base to combine with the acids or anhydrides, including chromate anhydride.

Chromites of calcian and magnesian metals precipitated by addition of ammonia to mixed chromic and calcian or magnesian salts. Composition of the calcium precipitate $2CaO.Cr_2O_3$. Ferrous chromite or chrome iron $FeO.Cr_2O_3$ or $FeCr_2O_4$, an analogous native compound. Replacement, in different specimens, of some ferrous oxide by magnesia and apparently by chromous oxide, and of some chromic oxide by ferric oxide and by alumina. Its occurrence crystallised in regular octahedrons; but, for the most part, in hard brownish-black granular veins or masses, of sp. gr. 4·5, usually imbedded in serpentine. Its insolubility in acids, difficult solution in fused borax to form a green bead, and oxidation by fusion with nitre and alkali carbonate to form a yellow mass yielding a yellow solution of alkali chromate.

Chromic chromate or brown oxide of chromium $Cr_2O_3.CrO_3$ or CrO_2, producible, both in anhydrous and hydrated

states, by various oxidations of chromic oxide, reductions of chromate anhydride, and precipitations of chromic salts by alkali chromates, &c. The anhydrous compound, formed as a dull brown powder, by gently heating chromic hydrate with access of air, or by keeping chromate anhydride for some time at 250°. The hydrate made by adding ammonia to mixed chromic chloride and potassium dichromate solutions. Production not of chromate oxichloride as with other chromates, but only of free chlorine as with manganic peroxide, by acting on either compound with sulphuric acid and common salt. The hydrate decomposible however by caustic alkali to furnish a soluble chromate.

Solubility of precipitated chromic hydrate in aqueous chromate anhydride to form a dark brown solution, apparently containing the normal salt $Cr_2O_3.3CrO_3$.

Sulphide, Cr_2S_3; not producible in moist way. Action of alkali sulphide on chromic solutions to precipitate hydrated chromic oxide and liberate sulphuretted hydrogen:

$$2CrCl_3 + 3(NH_4)_2S + 6H_2O = 6NH_4Cl + 3H_2S + Cr_2O_3.3H_2O$$

The anhydrous sulphide producible in plumbago-like black scales, by passing disulphide of carbon vapour over strongly ignited chromic oxide, or sulphuretted hydrogen over the ignited chloride.

Nitride, Cr_2N_2 or Cr_3N_4 (?); produced as a chocolate-brown powder, by heating anhydrous chromic chloride in current of ammonia. Its combustibility in air with bright red light, to yield chromic oxide and nitrogen with some nitric peroxide. Its dissolution in concentrated hydrochloric acid with production of chromic chloride and sal-ammoniac.

Nitrate, $Cr(NO_3)_3$; producible by dissolving chromic hydrate in nitric acid; not crystallisable; decomposible on ignition to leave brown oxide of chromium.

Sulphates. The soluble violet salt made by drenching chromic hydrate with oil of vitriol, and leaving mixture for some weeks exposed to the air. Production of a crystalline mass dissolving in water to form a blue solution yielding, upon addition

of alcohol, a deposit of violet crystals, having the formula $Cr_2(SO_4)_3.15Aq$. Solution of violet salt rendered green by ebullition and no longer precipitable by alcohol. Fusion of violet salt in its water of crystallisation at 100°, with loss of water, to leave the green salt $Cr_2(SO_4)_3.5Aq$. But by heating to 370°, a red crystalline anhydrous sulphate $Cr_2(SO_4)_3$, left, insoluble both in water and acids, but changing into the green soluble salt by prolonged ebullition. The green salt obtained in solution by boiling chromic oxide or hydrate in sulphuric acid, reducing the sulphuric acid solution of a chromate with sulphurous acid &c. Its production in form of an uncrystallisable mass, readily soluble in alcohol. Solution of green sulphate convertible into one of the violet sulphate by long keeping.

Direct combination of the soluble violet sulphate with potassium or ammonium sulphate to form chrome alum $KCr(SO_4)_2.12Aq$, a beautiful violet-red salt crystallising in octahedrons. Chrome alum readily produced by reaction of potassium dichromate and sulphuric acid in presence of some oxidisable substance, as alcohol or nascent hydrogen. Solution of chrome alum more stable than most violet chromic solutions, but convertible by ebullition into a dark green non-crystallisable liquid—stated by some, and denied by others, to contain free alkali sulphate from decomposition of the alum.

Oxalates. The double salts $K\overset{'''}{Cr}(C_2O_4)_2.4Aq$, and $K_3\overset{'''}{Cr}(C_2O_4)_3.3Aq$, produced by reduction of potassium dichromate solution with oxalic acid and with mixed potassium oxalate and oxalic acid respectively, the former in garnet-red tables, the latter in dark bluish prisms; the solutions of both salts being green by reflected, violet-red by transmitted light, and not precipitable by ammonia or, save upon ebullition, by potash:

$$K_2\overset{vi}{Cr_2}O_7 + 7H_2C_2O_4 = 2K\,\overset{'''}{Cr}(C_2O_4)_2 + 7H_2O + 6CO_2$$

$$K_2\overset{vi}{Cr_2}O_7 + 7H_2C_2O_4 + 2K_2C_2O_4 = 2K_3\overset{'''}{Cr}(C_2O_4)_3 + 7H_2O + 6CO_2$$

Chromic compounds recognisable in dry way by their green coloration of fused borax bead, and by their yielding a yellow

mass of soluble chromate when ignited with alkali carbonate and nitre. Chromic solutions recognisable by their violet or green colour, and by their giving with caustic potash a grey or green precipitate soluble in excess of potash, and reprecipitable of a green colour on boiling the solution.

CHROMOUS COMPOUNDS.

Chloride, $CrCl_2$. Perfectly dry sublimate of anhydrous chromic chloride gently heated in current of dry and air-free hydrogen until cessation of hydrochloric acid fumes:

$$Cr_2Cl_6 + H_2 = 2CrCl_2 + 2HCl$$

A white velvety substance left, retaining the form of the original sesquichloride, soluble in air-free water with evolution of heat and formation of a blue solution, quickly turning green from oxidation, and acting generally as a most powerful reducing agent. Production of a similar blue liquid by gradual solution of zinc in aqueous chromic chloride or sulphate, with some evolution of hydrogen.

Hydrate, $2CrO.H_2O$ or $Cr_2O(HO)_2$; thrown down by adding excess of potash to above solution of chromous chloride, as a yellow precipitate quickly becoming brown. Precipitate, having been quickly washed out of access of air with dilute potash and air-free ice-cold water, dried in a current of hydrogen. Its occurrence as a brown powder, but slowly alterable in dry state, insoluble in dilute, soluble in stronger acids, and decomposible by ignition with evolution of hydrogen and formation of chromic oxide:

$$Cr_2O(HO)_2 = Cr_2O_3 + H_2$$

The moist hydrate, as first thrown down, extremely unstable, becoming quickly changed into dark brown chromoso-chromic oxide $Cr_3O_4.H_2O$, by absorption of oxygen from the air, or even by gradual decomposition of water at ordinary temperatures with evolution of hydrogen.

Precipitation from chromous chloride solution, by ammonia, of

a pale blue ammoniacal compound dissolving in excess of ammonia and sal-ammoniac to form an unstable blue liquid. Precipitation by sulphide of ammonium of an unstable black chromous sulphide. Formation of chromous sulphate by solution of metallic chromium in dilute sulphuric acid. Formation of potassio-chromous sulphate $K_2Cr(SO_4)_2.6Aq$, by dissolving potassium sulphate in chromous chloride solution, adding alcohol to just short of producing a precipitate, and setting aside in a close vessel. Gradual deposition of a pale blue salt isomorphous with potassio-ferrous sulphate, potassio-zinc sulphate, &c. Characteristic absorption of nitric oxide gas by chromous as by ferrous solutions, with formation of dark brown compounds.

(86.) MOLYBDENUM.

Its occurrence as lead molybdate $PbMoO_4$, in wulfenite; and as molybdous sulphide MoS_2, in molybdenite. Its production in metallic state by reduction of molybdic anhydride with charcoal or hydrogen at a strong heat. Grey pulverulent mass; or, after fusion by most intense heat of blast furnace, a lustrous, silver-white, very hard metal, of sp. gr. 8·6. The pulverulent metal oxidisable at a gentle heat in air. Molybdenum attackable by nitric acid with successive formation of molybdous nitrate and molybdic anhydride. Its ready oxidation by fusion with nitre to yield potassium molybdate. Its indifference to boiling hydrochloric acid.

Formation by molybdenum of a well defined series of molybdic or hexad compounds, typified by the oxichloride MO_2Cl_2, and the anhydride MoO_3; a less complete series of molybdous or tetrad compounds typified by molybdous chloride $MoCl_4$, and the sulphide MoS_2; and an imperfectly known series of hypomolybdous or diad compounds typified by hypomolybdous chloride $MoCl_2$, &c.

MOLYBDIC COMPOUNDS.

Oxichloride, MoO_2Cl_2; produced by passing chlorine gas over the heated dioxide; and in other ways. Volatile, yellowish,

crystalline scales, soluble in water, with decomposition into hydrochloric and molybdic acids.

Oxide or anhydride, MoO_3; occasionally found native, in earthy or crystalline state, as molybdine; produced as a crystalline sublimate by heating small lumps of molybdic disulphide MoS_2, in glass tube with current of air drawn through it; also as a pulverulent residue by heating the sulphide in an open crucible; and by gently heating molybdate of ammonium. Molybdic anhydride usually met with as a loose, white, pulverulent mass, breaking up into small scales when shaken with water. Its fusion below a red heat into dark yellow liquid, solidifying as a pale yellow crystalline mass, and furnishing when slowly cooled distinct crystals. Its fixity when heated in close vessels, but ready volatilisation in current of air. Its solubility in caustic and carbonated alkalis with formation of molybdates. Sparing solubility of the unignited anhydride in water, to form a liquid of slightly acid reaction and metallic taste, capable after acidification of giving a red precipitate with ferrocyanide of potassium. Production of freely soluble colloid molybdic anhydride by dialysing solution of sodium molybdate in aqueous hydrochloric acid. Compound left, on desiccation at 100°, in anhydrous, soluble, non-crystalline gummy scales.

Solubility of unignited molybdic anhydride in most of the stronger acids, to yield incompletely examined saline products. Its solubility, before and even after ignition, in cream of tartar to form a sort of tartar-emetic. Compound of molybdic anhydride with common phosphoric acid known as phospho-molybdic acid. Salts of this compound acid with ammonia and vegeto-alkalis characterised by their insolubility, and yellow colour. In presence of hydrochloric acid, ammonia and vegeto-alkalis precipitated by phospho-molybdate of sodium, and phosphoric acid precipitated by molybdate of ammonium.

Molybdates. For the most part colourless salts; those of the alkali metals and ammonium readily soluble. Precipitation, on acidifying their neutral or alkaline solutions, of acid molybdates, and afterwards of molybdic anhydride, soluble in excess

of the precipitant. Neutral ammonium molybdate $(NH_4)_2MoO_4$, thrown down by addition of alcohol to solution of molybdic anhydride in excess of ammonia. Crystallisable acid salt $(NH_4)HMoO_4$, produced by evaporation of above solution. Potassium molybdate made by dissolving molybdic anhydride in carbonate of potassium solution. Separation from the liquid, after addition of acid thereto until production of slight permanent precipitate, of complex crystalline salt decomposible by water into freely soluble mono-molybdate K_2MoO_4, and sparingly soluble but crystallisable tri-molybdate $K_2Mo_3O_{10}.3Aq$. Insoluble molybdates made by precipitation; or, in crystalline state, by fusing molybdic anhydride with chloride of the precipitable metal and common salt. Lead molybdate $PbMoO_4$, found native as wulfenite, in grey or yellow square octahedrons or tables.

Sulphide, MoS_3; a well-characterised sulphur anhydride, thrown down as a brown-black precipitate on acidifying solutions of alkali sulphomolybdate. Its re-solution in alkali and alkaline-earth monosulphides and sulphydrates to form crystallisable sulpho-salts. Its conversion into the disulphide MoS_2, by heat. Alkali sulphomolybdates best made by passing sulphuretted hydrogen into solutions of the corresponding molybdates. Dull red liquids yielding crystals, as of K_2MoS_4, on evaporation out of contact with air; and precipitating corresponding compounds of the heavy metals from their dissolved salts.

MOLYBDOUS COMPOUNDS.

Chloride, $MoCl_4$; made by heating molybdenum or its sulphide in a current of air-free chlorine. A red vapour, condensing in fusible, deliquescent, iodine-like crystals. Its dissolution in water attended with great development of heat, and production of a brown liquid. Similar aqueous chloride obtainable by reducing hydrochloric acid solution of molybdic anhydride with molybdenum, and in other ways. Absorption of atmospheric oxygen by the dilute solutions, with change from red-brown to blue colour.

Oxide, MoO_2; made by gently heating molybdic anhydride in a current of hydrogen; also by drying the hydrated oxide in vacuo. A red-brown powder, indifferent to most reagents, but oxidisable by nitric acid and absorptive of chlorine to form the oxichloride. The hydrated compound thrown down by excess of ammonia from above solutions of the chloride. A rust-coloured precipitate, *insoluble in caustic alkali, insoluble in saline solutions, slightly soluble in pure water to form a red liquid of faintly acid reaction, gelatinising after some weeks.* Oxidation of the moist hydrate on exposure to air, with production of a more soluble blue compound. Molybdous salts made by dissolving the hydrated oxide in acids: by reducing acid solutions of molybdic anhydride with molybdenum, copper, &c.; and by dissolving metallic molybdenum in acid, with aid of some oxygenant as nitric acid or molybdic anhydride. Molybdate of molybdenum $MoO_2.4MoO_3$ or $\overset{''}{Mo}(Mo_2O_7)_2$, thrown down as a deep blue hydrate on adding molybdous chloride to molybdate of ammonium. Compound scarcely soluble in sal-ammoniac, somewhat soluble in water. Its production also by oxidising molybdous oxide or its salts, and by reducing molybdic oxide or anhydride.

Sulphide, MoS_2; or molybdenite, the principal ore of molybdenum, originally mistaken for plumbago. A sectile, soft, flexible, and elastic mineral, of metallic aspect, and leaden colour, occurring in laminated semi-crystalline masses, and occasionally in hexagonal tables. Its unalterability by heat alone, but conversion by roasting into molybdic anhydride.

HYPOMOLYBDOUS COMPOUNDS.

Action of zinc and other oxidisable metals upon hydrochloric acid solution of molybdic anhydride to produce in succession the intermediate blue compound, the red brown molybdous chloride $MoCl_4$, and finally an almost black hypomolybdous chloride $MoCl_2$. Production from above solution of hydrated hypomolybdous oxide MoO, by cautious addition of ammonia (so as not to throw down the zinc) and digestion of resultant black precipi-

tate in excess of ammonia. Its solution, though with some difficulty, in acids to form non-crystallisable salts.

(87.) TUNGSTEN.

Tungsten met with principally as ferrous tungstate $FeWO_4$, in wolfram; as calcium tungstate $CaWO_4$, in scheelite; and as lead tungstate $PbWO_4$, in scheeletine. Tungsten obtained as an iron-grey metallic mass, by intense ignition for some hours of tungstic anhydride intimately mixed with lamp-black. So-produced metal extremely hard and difficultly fusible; of sp. gr. 17·6; capable of being heated in air without change; attackable, with production of tungstic anhydride or tungstates, by nitric or nitro-muriatic acid, and by fused caustic alkali or nitre. Tungsten also obtained in pulverulent state by strongly heating the anhydride in a current of hydrogen. Dark-grey powder, rendered lustrous by burnishing, combustible when heated in air, and attackable by aqueous alkalis.

Formation by tungsten of a well-defined series of hexad or tungstic compounds typified by the chloride WCl_6, the chloroxide WCl_4O, the oxichloride WCl_2O_2, and the oxide or anhydride WO_3. Existence also of an inferior or tetrad series of tungstous compounds, and of a few intermediate products.

TUNGSTIC COMPOUNDS.

Chloride, WCl_6; made by heating tungsten in perfectly dry air-free chlorine gas; and, together with succeeding compounds, by passing chlorine over ignited mixture of tungstic oxide and charcoal. Dark violet scales, fusing at 183°, into a bronze-like mass, volatilising at a higher temperature to furnish a dark red vapour, condensable with care in crystalline state. Its difficult production and preservation in entirely unoxidised condition by reason of its liability to change into the chloroxide, at ordinary temperatures by action of moist air with correlative production of hydrochloric acid, and at increased temperatures by action of dry air with correlative evolution of chlorine.

Chloroxide, WCl_4O; produced by passing chlorine over ignited mixture of tungstic anhydride with deficit of charcoal; and together with the chloride and oxichloride in processes for their preparation, &c. A light scarlet, frequently crystalline sublimate, readily fusible and volatile.

Oxichloride, WCl_2O_2; most easily prepared by heating tungstous oxide WO_2, in chlorine gas, and formed in above processes together with preceding compounds. Golden yellow scales, volatile without fusion at 265°.

Differentiation and relationship of the three tungstic chlorides but imperfectly made out. Decomposition of all three compounds by excess of water, with production of hydrochloric and tungstic acids.

Oxide or anhydride, WO_3; made by igniting tungstic acid or tungstate of ammonium. An insoluble yellow powder, becoming temporarily darker by heat, fusing in forge fire, and volatilising in oxihydrogen flame. Its insolubility in acids; solubility in caustic alkalis, and in carbonated alkalis with effervescence of carbanhydride. Its reduction to metallic state by ignition with hydrogen or charcoal.

Hydrate or acid, H_2WO_4 or $H_2O.WO_3$. Scheelite treated with hydrochloric acid, or wolfram with nitro-hydrochloric acid. Residuary crude tungstic acid dissolved in ammonia, and thrown down in pure state on acidifying the solution. Its precipitation in the cold as a white bulky hydrate $H_2WO_4.Aq$, and at boiling heat as a dense yellow powder H_2WO_4. Its behaviour with acids and alkalis similar to that of the anhydride. Existence of a variety of tungstic acid, known as metatungstic acid, soluble in water (*vide infra*).

Tungstates. Ordinary tungstates, except those of alkali-metal, ammonium, and magnesium, insoluble in water and procurable by precipitation. Also, including the magnesium salt, procurable in crystalline state by fusing sodium tungstate with chloride of the other metal, sometimes in admixture with chloride of sodium.

Calcium tungstate, $CaO.WO_3$, producible as above; and found

native as scheelite, in reniform masses and crystallised in quadratic octahedrons.

Lead tungstate, $PbO.WO_3$, producible as a white precipitate; found native as scheeletine, in greenish quadratic tables and octahedrons isomorphous with those of wulfenite.

Ferrous tungstate, $FeO.WO_3$, found native as wolfram, with from $\frac{1}{6}$ to $\frac{1}{4}$ of its iron habitually replaced by manganese. Its occurrence as a dense, brownish-black, lustrous mineral, in massive state and crystallised in orthorhombic prisms. Principal alkali tungstates formulated below. Existence of other and very complex acid salts:

Normal Tungstates.	Acid Tungstates.
$K_2O.WO_3$	$K_5H_3O_4.6WO_3.4Aq$
$Na_2O.WO_3$	$Na_5H_3O_4.6WO_3.12 \& 18Aq$
	$(NH_4)_5H_3O_4.6WO_3.4 \& 1Aq$

The sodium and potassium normal salts made by fusing powdered wolfram with alkali carbonate; or by dissolving tungstic oxide in boiling solution of the carbonate. Both salts soluble in water, insoluble in alcohol, crystallisable in differently hydrated states, producible in anhydrous state by heat, and fusible at an incipient red heat. Ordinary potassium salt the monohydrate $K_2O.WO_3.Aq$, crystallising in needles; ordinary sodium salt the dihydrate $Na_2O.WO_3.2Aq$, crystallising in rhombic tables.

The acid sodium and potassium salts made by fusing tungstic oxide with the normal salts, and crystallising the products from water. Also, from solutions of the normal salts, by boiling them with tungstic oxide, or treating them with mineral acid, and preferably with a current of carbanhydride. The ammonium salt made by dissolving tungstic oxide in excess of ammonia and crystallising. The potassium and ammonium salts but sparingly, the sodium salt freely soluble. By fusing the sodium salt and lixiviating the product with water, an insoluble residue left of the anhydrous compound $Na_2O.4WO_4$.

Production, on boiling gelatinous silica in solution of the acid

potassium or sodium salt, of a crystallisable silico-tungstate, with exchange of silicon for alkali-metal:

$$\left.\begin{array}{l}2(K_3H_3O_4.6WO_3)\\ \text{or } K_{10}H_6O_8.12WO_3\end{array}\right\} + 2H_2\overset{iv}{Si}O_3 = K_8\overset{iv}{Si}O_6.12WO_3 + K_2SiO_3 + 5H_2O$$

The acid silico-tungstate $K_4H_4\overset{iv}{Si}O_6.12WO_3$, obtained in large hexagonal prisms, on crystallising the neutral salt from dilute hydrochloric acid. Mercurous silico-tungstate thrown down, from the neutral alkali-metal salt, by mercurous nitrate, as a yellow precipitate yielding silico-tungstic acid by its decomposition with hydrochloric acid. The silico-tungstic a soluble, crystallisable, powerful acid, decomposing carbonates with effervescence, and forming numerous soluble and crystallisable salts, the mercurous salt being alone insoluble. Existence of other series of silico-tungstic compounds.

Metatungstates. Above soluble tungstates, acid and neutral, decomposible by excess of nitric or hydrochloric acid with immediate precipitation of tungstic acid. Existence of another class of tungstates or meta-tungstates not precipitable on acidification. Potassium metatungstate $K_2O.4WO_3.8Aq$, obtained by boiling solution of the ordinary tungstate for some time with tungstic acid in state of white hydrated precipitate, until rendered no longer precipitable by nitric acid. Its crystallisation on evaporation in quadratic octahedrons. The sodium and ammonium salts produced in a similar manner. Barium metatungstate $BaO.4WO_3.9Aq$, formed by precipitation. Its decomposition by exact sufficiency of sulphuric acid to yield solution of metatungstic acid, obtainable in crystalline state by cautious evaporation. The meta-tungstates at once reconvertible into ordinary tungstates by addition of alkali.

Sulphide, WS_3; obtained, as a dark brown or black precipitate, by dissolving tungstic acid in aqueous potassium sulphide and acidifying the solution. Its action as a sulphanhydride, and dissolution in alkali sulphides to form sulpho-tungstates, also producible by treating the oxy-tungstates with sulphuretted hydrogen. The potassium salt $K_2S.WS_3$ or K_2WS_4, crystal-

lisable in red prisms. An oxisulpho-tungstate $K_2WS_2O_2.2Aq$, crystallisable in brown-yellow tables.

TUNGSTOUS COMPOUNDS.

Chloride, WCl_4; produced, as a brownish black mass, by passing hydrogen over gently heated tungstic chloride. Its decomposition by water to yield tungstous oxide and hydrochloric acid.

Oxide, WO_2; produced, as a brown combustible powder, by reducing tungstic anhydride with hydrogen at a low red heat. Also in coppery red crystalline scales, by acting on the anhydride with zinc and hydrochloric acid. Tungstous oxide not reactive with acids to produce salts. Its solubility in strong caustic alkali, with evolution of hydrogen and formation of a tungstate:

$$2KHO + WO_2 = K_2O.WO_3 + H_2$$

Peculiar tungstous compound $Na_2W_2O_5$ or $Na_2O.2WO_2$, having a striking resemblance to metallic gold, made by fusing sodium tungstate with tungstic anhydride, acting on the product at a red heat with hydrogen, and washing away soluble salts. Lustrous golden yellow cubes and plates left, undecomposible by sulphuric or nitro-muriatic, but yielding to hydrofluoric acid.

An intermediate tungstous oxide $WO_2.WO_3$ or W_2O_5, produced as a fine blue powder, by heating tungstate of ammonia to redness in a retort. Same compound produced in the moist way by incomplete reduction of tungstic acid with stannous chloride, or with metallic tin or zinc in presence of dilute sulphuric or hydrochloric acid. Reaction employed as a means of reçognising tungstic acid.

Sulphide, WS_2; obtained by heating mixture of tungstic acid, or acid tungstate of potassium, with sulphur in a covered crucible, as soft, black, needle-shaped crystals, having very much the appearance and physical properties of plumbago.

Phosphide, W_3P_4; produced, as a dark grey powder, by

passing phosphorus vapour over ignited tungsten. Its seriation with the preceding tungstous compounds, thus: WCl_4, W_2S_4 (or $2WS_2$), W_3P_4. Another phosphide W_4P_2, formed by igniting tungstic anhydride, mixed with excess of phosphoric acid, in a charcoal-lined crucible. Its occurrence in geode-like masses, made up of hexagonal prisms an inch or so long, of lustrous steel-grey colour, sp. gr. 5·2, conductive of electricity, unattackable by acids, incombustible in air, but combustible with great splendour in oxygen.

CHAPTER XI.

(88.) IRON ELEMENTS.

MANGANESE, Iron, Cobalt, Nickel, Copper.

Permanent, but readily oxidisable metals, associated with one another by their analogous series of corresponding diad chlorides, oxides, sulphates, $\overset{''}{M}Cl_2$, $\overset{''}{M}O$, $\overset{''}{M}SO_4$, &c., very similar in properties to each other, and, for the most part, isomorphous with each other, and with corresponding compounds of zinc and magnesium. Symbols and atomic weights:

Mn	Manganese	55
Fe	Iron	56
Co	Cobalt	59
Ni	Nickel	59
Cu	Copper	63·5

Resemblance of metals to one another manifested chiefly by their diad compounds. Soluble diad salts of manganese and cobalt characterised by a pink or violet colour. Soluble diad salts of iron, nickel, and copper characterised by a green or blue colour. Remarkable parallelism in properties of cobalt and nickel. Seriation in properties of iron, nickel, and copper.

In addition to the formation by each metal of occasional compounds pertaining to different non-diad series of compounds, formation by copper of a well-defined and tolerably complete series of monad or quasi-monad compounds, exemplified by cuprous chloride $CuCl$ or Cu_2Cl_2, and oxide Cu_2O, very similar in their properties to, and frequently isomorphous with, the corresponding compounds of silver.

Formation by iron of a well-defined triad or quasi-triad series of compounds, exemplified by ferric chloride $FeCl_3$ or Fe_2Cl_6, very similar in their properties to, and for the most part isomorphous with, corresponding chromic and aluminic compounds. Also of an incomplete series of unstable hexad compounds, exemplified by ferrate of potassium K_2FeO_4, analogous to chromate of potassium K_2CrO_4, sulphate of potassium K_2SO_4, &c.

Formation, by manganese also, of two incomplete and unstable series of compounds analogous to the above two series of iron compounds; and, in addition, of a well-defined and tolerably stable series of heptad compounds, exemplified by permanganate of potassium $KMnO_4$, corresponding to and isomorphous with perchlorate of potassium $KClO_4$.

Uranium a rare and peculiar metal without obvious analogues, but usually classified with iron. Combination of 60 parts of uranium with 35·5 parts of chlorine to form a volatile green uranous chloride, usually represented as a di-chloride by formula UCl_2, the atomic weight of uranium being taken as 120. Existence also of a higher series of yellow uranic compounds, typified by uranic oxide U_2O_3, and oxichloride $\ddot{U}OCl$.

(89.) Manganese.

Manganic peroxide MnO_2, the chief source of manganese compounds, found abundantly both in amorphous and crystalline forms as pyrolusite; also met with in an impure hydrated condition as wad. Frequent occurrence also of native manganic oxide Mn_2O_3, in anhydrous state as braunite, in hydrated state as manganite $H_2Mn_2O_4$, and combined with manganous oxide as hausmannite $\ddot{M}nMn_2O_4$ or Mn_3O_4. Manganese further met with in form of manganous sulphide MnS, as manganese-blende; of arsenide MnAs, as mangan-arsenide or kaneite; of carbonate $MnCO_3$, as diallage or brown-spar; and as silicate Mn_2SiO_4, in tephroite, knebelite, &c. Frequent presence of more or less manganese in very many minerals, more especially

in different iron-ores, and in magnesian and alumino-magnesian silicates.

Manganese but little known in the metallic state. Button of greyish-white, iron-like, metal obtained by exposing an intimate mixture of artificial manganic oxide and lamp-black to intense heat in a charcoal-lined crucible. Manganese so produced, a feebly magnetic metal, of sp. gr. 8·0, fine-grained in texture, brittle and cleavable. Its fusion only in strongest heat of a blast furnace. Its rusting in moist air; slow decomposition of water at ordinary temperatures, and ready dissolution in dilute hydrochloric or sulphuric acid with evolution of hydrogen.

Formation by manganese of four distinct series of compounds; a diad or manganous series, typified by manganous chloride $MnCl_2$; a triad or quasi-triad or manganic series, typified by manganic oxide Mn_2O_3, and manganese alum $K\overset{'''}{Mn}(SO_4)_2.12Aq$; a hexad or manganate series, typified by potassium manganate K_2MnO_4 or $K_2O.MnO_3$; and a heptad or quasi-heptad or permanganate series, typified by potassium permanganate $KMnO_4 = \frac{1}{2}(K_2O.Mn_2O_7)$. Existence also of manganic peroxide MnO_2, and of several intermediate compounds.

MANGANOUS COMPOUNDS.

Chloride, $MnCl_2$; obtained by heating the mono-hydrate, preferably in atmosphere of hydrochloric acid. A rose-coloured compound, fusible out of access of air at a dull red heat, and solidifiable into a lamellar mass. Its decomposition when heated in a current of air, and especially of moist air, to become manganoso-manganic oxide Mn_3O_4. Its deliquescence in moist air, hydration by water with evolution of heat, and solubility in water to form a pale-pink solution of the hydrated chloride $MnCl_2.4Aq$, obtained in pale-rose prismatic crystals, either by cooling of the hot concentrated solution or by spontaneous evaporation of the cold solution. Its conversion, by desiccation at 100°, into the pulverulent mono-hydrate $MnCl_2.Aq$. Both compounds deliquescent in moist air. Manganous chloride formed in solution by

dissolving manganic peroxide, or any form of manganese oxide or carbonate, in hydrochloric acid at a boiling heat:

$$MnO_2 + 4HCl = 2H_2O + MnCl_2 + Cl_2$$

About one-fourth of the solution precipitated by carbonate of sodium, and resulting crude manganous carbonate boiled with other three-fourths, to precipitate the iron always present in manganese oxides and crude products obtained therefrom:

$$Fe_2Cl_6 + 3MnO.CO_2 + H_2O = 3MnCl_2 + Fe_2O_3.H_2O + 3CO_2$$

Solution of manganous chloride not affected by passage of chlorine gas through it. Combination of manganous chloride with sal-ammoniac and alkali-metal chloride, to form crystallisable double salts.

Oxide, MnO; obtained by igniting manganous carbonate or oxalate in a current of hydrogen. An olive-green powder, oxidisable on mere exposure, and combustible on ignition, into the $\frac{3}{4}$-oxide. The hydrated oxide thrown down from manganous salts, by caustic alkali, as a white precipitate, quickly becoming brown through oxidation. Its solubility in sal-ammoniac and ammonia to form a colourless solution, yielding a brown precipitate of higher oxide on exposure to air.

Sulphide, MnS; found native as manganese-blende, massive and crystallised in cubes and octahedrons. Producible in hydrated state, as a pale buff precipitate, by reaction of alkali sulphide or sulphydrate and manganous salts. Its browning, through oxidation, on exposure to air; and ready solution even in weakest acids to form manganous salts. An arsenide of manganese, corresponding to the sulphide, found native in botryoidal masses as kaneite, MnAs or Mn_2As_2.

Carbonate, $MnCO_3$; found native as diallage or brown-spar, in rhombohedral crystals isomorphous with those of talc-spar. Produced in hydrated state $2MnCO_3.Aq$, by precipitating manganous solutions with fixed alkali carbonate. An opaque white precipitate soluble, as first thrown down, in sal-ammoniac solution. Com-

pound not oxidisable by mere exposure, rendered anhydrous by a moderate heat, converted by gentle ignition in air into the $\frac{3}{4}$-oxide.

Sulphate, $MnSO_4$; made by dissolving the native peroxide, sometimes partially reduced by previous ignition with coal-dust, in sulphuric acid, evaporating solution to dryness, and igniting the residue to effect decomposition of its iron sulphate. Manganous sulphate then dissolved out from the ignited mass, and crystallised from resulting solution. Its deposition in pale rose-coloured crystals, with 7, 6, 5, 4, and 2 atoms of water according to circumstances. The hepta-hydrated salt isomorphous with ordinary green or iron vitriol, and the pentahydrate with blue or copper vitriol. The tetrahydrate the most commonly produced salt. Its crystallisation from solution, between 20° and 30°, in clino-rhombic prisms, isomorphous with those of tetrahydrated ferrous sulphate. Salt rendered monohydrated at 115°, not further altered up to 200°, above which point rendered anhydrous. The anhydrous compound unaffected even by strong ignition. Combination of manganous sulphate, as of ferrous, cobalt, nickel and cupric sulphates, with sulphate of potassium, sulphate of ammonium, &c., to form crystallisable hexahydrated double salts as $K_2Mn(SO_4)_2.6Aq$, isomorphous with magnesian double sulphates.

Dithionate, MnS_2O_6; prepared by passing sulphurous anhydride through finely divided manganic peroxide suspended in water, kept cold during the reaction to prevent formation of sulphate:

$$MnO_2 \quad + \quad 2SO_2 \quad = \quad MnS_2O_6 \quad \text{or} \quad MnO.S_2O_5$$

Salt employed as the usual source of dithionate compounds. Its deposition on spontaneous evaporation in rose-coloured, deliquescent, hydrated crystals.

Solutions of manganous salts either white or pale rose-coloured; characterised by giving with sulphide of ammonium a buff precipitate easily soluble in dilute acids; with potash a white precipitate becoming brown on exposure; and with ammonia and

sal-ammoniac a white precipitate dissolving in excess of the precipitant to form colourless solutions speedily becoming brown and opaque on exposure to air.

MANGANIC COMPOUNDS.

Chloride, $MnCl_3$ or Mn_2Cl_6; a scarcely known substance produced, in form of brown solution, by dissolving finely divided manganic oxide or hydrate little by little in cold concentrated hydrochloric acid. Its decomposition, gradually on keeping, rapidly on ebullition, into manganous chloride and free chlorine.

Oxide, Mn_2O_3; found native as braunite, in obtuse quadratic octahedrons, of brownish-black colour and sp. gr. 4·8. Produced artificially, as a black powder, by heating manganic hydrate or peroxide to low redness. Its reduction by strong ignition to leave the $\frac{3}{4}$-oxide. Its reactions, when heated with nitric and dilute sulphuric acids, to form manganous salts and leave manganic peroxide; when heated with strong sulphuric acid, to form manganous sulphate and oxygen:

$$MnO.MnO_2 \text{ or } Mn_2O_3 + H_2SO_4 = H_2O + MnSO_4 + MnO_2$$
$$Mn_2O_3 + 2H_2SO_4 = 2H_2O + 2MnSO_4 + O$$

Its dissolution by concentrated hydrochloric acid, in the cold to form brown manganic chloride, at a boiling heat to form manganous chloride and chlorine.

Hydrate, $H_2O.Mn_2O_3$ or $H_2Mn_2O_4$; found native as manganite, in dark reddish brown orthorhombic crystals, of sp. gr. 4·2. Produced artificially by subjecting precipitated manganous hydrate to current of air, or the carbonate to chlorine in deficit, and dissolving away any unaltered manganous compounds with very dilute nitric acid. A soft dark-brown powder, rendered anhydrous below a red heat. Its reactions with nitric and hydrochloric acids similar to those of the oxide. Its combinations with sulphuric and phosphoric acids to form manganic salts.

Manganoso-manganic oxide, $MnO.Mn_2O_3$ or Mn_3O_4; found native as hausmannite, in brownish-black acute quadratic octahedrons, of sp. gr. 4·7. Its artificial production as a dull reddish powder, by strongly igniting any oxide, hydrate, nitrate, carbonate, or oxalate of manganese—the manganous compounds with exposure to air. Its reactions similar to those of the sesquioxide.

Manganic salts, for the most part unstable and but little known. Their colour violet when hydrated, brownish-green when anhydrous, whether through desiccation or presence of strong hydrochloric or sulphuric acids. Violet solutions mostly decomposed on dilution, with precipitation of manganic hydrate and separation of free acid. The sulphate $Mn_2(SO_4)_3$, formed by mixing artificial manganic peroxide into a paste with oil of vitriol, heating the mass to 135°, washing product with strong nitric acid, and drying the residue at 130°. A dark green amorphous powder, rapidly deliquescing and forming an unstable violet solution decomposing at once on dilution. Manganic hydrate, containing some manganous hydrate, soluble in slightly diluted sulphuric acid to form a reddish violet solution, yielding on admixture with potassium sulphate and careful evaporation, violet octahedral crystals of manganese alum $KMn(SO_4)_2.12Aq$, decomposible into manganic hydrate and acid sulphate of potassium, &c., on admixture with water. Production of an acid manganic phosphate $\overset{'''}{Mn}PO_4.xH_3PO_4$, in form of a stable violet-blue solution, by evaporating down mixed manganic peroxide and aqueous phosphoric acid, evaporating to syrupy consistency, and diluting the product with water.

Manganic peroxide, MnO_2; found native as pyrolusite, in steel-grey orthorhombic prisms, of sp. gr. 4·8 or 4·9; and in granular and massive states. Several descriptions of earthy manganese, as psilomelane, wad, &c., also met with in form of brown-black masses, containing variable proportions of inferior manganese oxides, water of hydration, &c. Varvacite a laminated semicrystalline mineral, formulated as $\left.\begin{matrix}MnO\\H_2O\end{matrix}\right\} 3MnO_2$. Man-

ganic peroxide, in anhydrous and hydrated states, produced artificially by many processes. The anhydrous oxide most readily made by heating the carbonate to 260°, with free exposure to air, and if requisite washing out any unaltered carbonate with dilute nitric acid. Process sometimes employed on manufacturing scale:

$$MnO.CO_2 \;+\; O \;=\; MnO_2 \;+\; CO_2$$

A hydrate $H_2O.MnO_2$, producible by decomposition of alkali manganate solutions; by precipitation of manganous solutions with peroxide of hydrogen; by subjecting manganous carbonate, suspended in water, to full action of chlorine, &c. The precipitate formed in manganous solutions by mixed hypochlorite and hydrate (as bleaching powder) said to be the hydrate $H_2O.2MnO_2$; and product left on treating manganoso-manganic oxide with nitric acid said to be the hydrate $H_2O.4MnO_2$. Similar combination of manganic peroxide with bases as with water. The calcium compound $CaO.xMnO_2$, produced on manufacturing scale by blowing air through mixed manganous hydrate and milk of lime.

Manganic peroxide conductive of electricity, strongly electronegative in voltaic current, and used accordingly in the construction of dry and other voltaic piles. Its decomposition by ignition, to leave manganic or manganoso-manganic oxide according to temperature, &c. Its behaviour as a manganous manganate when heated with caustic potash in close vessels:

$$\left.\begin{array}{l}2MnO_2 \text{ or} \\ MnO.MnO_3\end{array}\right\} \;+\; 2KHO \;=\; \left.\begin{array}{l}K_2MnO_4 \text{ or} \\ K_2O.MnO_3\end{array}\right\} \;+\; MnO \;+\; H_2O$$

Indifference of the peroxide to nitric acid. Its combination with sulphurous acid or anhydride to form manganous dithionate. Its reactions, when heated with strong hydrochloric acid to evolve chlorine, and with strong sulphuric acid to evolve oxygen. Manganic peroxide, with sulphuric acid in more or less dilute state according to circumstances, in constant use as an oxidising mixture. Complete oxidation of oxalic acid by the peroxide, in

presence of even very dilute sulphuric acid to take up the reduced manganous oxide:

$$H_2C_2O_4 + MnO_2 = H_2O + 2CO_2 + MnO$$

Reaction employed as a means of estimating the amount of peroxide contained in commercial samples. Important use of manganic peroxide in manufacture of chlorine and bleaching powder. Also, in plate-glass manufacture, to discharge the different greenish tints, consequent on presence of ferrous silicate in the glass. Liability of over-manganesed glass to become purple on exposure to light.

Reaction of manganic, and, owing to their oxidation, of manganous compounds, heated with borax bead in oxidising flame, to produce an amethyst colour, interfered with by presence of much iron, and disappearing in the reducing flame.

MANGANATES.

Production by heating manganese compounds with carbonate of sodium or potassium in oxidising flame, or preferably with mixed carbonate and nitrate, of a fused mass coloured deep green by presence of alkali manganate. Reaction employed as a valuable test for manganese. Manganate of potassium K_2MnO_4, best made on small scale by Gregory's process. Finely powdered mixture of manganic peroxide and chlorate of potassium added to strong caustic potash solution. Resulting paste dried by heat, and powdered mass ignited in platinum crucible at temperature insufficient to effect its fusion. Or, according to Béchamp, dried-up mixture of manganic peroxide and strong caustic potash, reduced to powder, and heated to dull redness in current of air. Dissolution of either crude product in moderate quantity of water, to form a dark green solution. Salt obtainable in dark green almost black crystals, isomorphous with those of potassium sulphate, chromate, &c., by evaporating the concentrated solution in vacuo, over oil of vitriol. In absence of excess of alkali, manganate of potassium decomposed by water, with production

of red permanganate solution and deposition of hydrated manganese peroxide:

$$3K_2MnO_4 + 3H_2O = 2KMnO_4 + 4KHO + H_2O.MnO_2$$

Alkaline solution of the crude manganate similarly decomposible by dilution, ebullition, or treatment with carbonic acid. But formation of a manganous salt instead of manganic peroxide, by addition of stronger mineral acids to the green solution:

$$5K_2MnO_4 + 4H_2SO_4 = 4KMnO_4 + MnSO_4 + 3K_2SO_4 + 4H_2O$$

Barium manganate produced, as a green insoluble powder, by adding manganic peroxide to fused mixture of chlorate of potassium and hydrate of barium. Sodium manganate, in solution (Condy's green fluid), made on large scale by keeping mixture of manganic peroxide and caustic soda at dull red heat for forty-eight hours in shallow vessels, and extracting product with water. Salt very soluble, and not crystallisable.

Employment of manganate solutions as oxidising and deodorising agents. Their reduction effected by most forms of organic matter. Their incapability even of being filtered through paper without suffering some decomposition.

PERMANGANATE COMPOUNDS.

Salts far more stable than the manganates. Potassium permanganate made by boiling up Gregory's crude manganate with water, and converting solution into one of the permanganate by addition of dilute nitric or sulphuric acid, or by treatment with carbonic acid, or by simple ebullition and evaporation. Resulting red solution, freed in two latter cases from precipitate of peroxide by decantation or filtration through asbestos, evaporated down and product purified by recrystallisation.

Crystallisation of potassium permanganate $KMnO_4$, in anhydrous dark purple-red orthorhombic prisms, frequently of considerable size; isomorphous with those of potassium per-

chlorate $KClO_4$. Salt decomposible by heat, to leave mixture of potassium manganate and manganic peroxide:

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2$$

Its deflagration, when heated or triturated with sulphur and other combustible bodies. Its solubility in 16 parts of cold water to form a deep purple-red solution. Potassium permanganate solution readily reducible, in presence of free acids, to state of colourless manganous salt; and accordingly in constant laboratory use for the volumetric estimation of oxidisable compounds both mineral and organic. In presence of alkali, the permanganate solution reducible at first to state of green manganate. Use of alkaline permanganate solution in water analysis, by Wanklyn and Chapman, to change nitrogenous organic matter into ammonia, estimatable by Nessler's test. Sodium permanganate not producible in crystalline state. Silver permanganate $AgMnO_4$, gradually separated in crystalline state from mixture of warm nitrate of silver and permanganate of potassium solution. Barium permanganate $Ba(MnO_4)_2$, made by acting on the manganate, suspended in water, with current of carbanhydride; or by decomposing above silver salt with chloride of barium. Its crystallisation, on evaporation of solution, in almost black prisms isomorphous with those of anhydrous sodium sulphate Na_2SO_4. Hydrogen permanganate, or permanganic acid $HMnO_4$, evidently a compound of considerable stability, though as yet but imperfectly examined. Its alleged production in form of a reddish-brown crystalline mass, yielding a violet solution, by decomposing barium permanganate with exact sufficiency of aqueous phosphoric acid and evaporating down. Also, in form of violet vapours condensing into a greenish black liquid, by cautiously heating to 60° or 70°, a mixture of potassium permanganate and the hydrate of sulphuric acid $H_2SO_4.H_2O$. Its deliquescence and formation of a dark violet solution. Its detonation when briskly, volatilisation when gradually heated. Its oxidations, as of alcohol, paper, &c., often attended with detonation and combustion.

(90.) IRON.

Iron one of the most abundant and widely distributed of elements. Native iron, alloyed with a variable proportion of nickel and traces of other metals, met with as meteoric iron, either in separate masses or distributed in the substance of composite meteorites. Rare occurrence also of native telluric iron, in grains and plates of considerable ductility and malleability. Chief sources of iron its different oxidised compounds, namely, spathic ore or ferrous carbonate $FeCO_3$; brown-ore or ferric hydrate $3H_2O.2Fe_2O_3$; red hæmatite or ferric oxide Fe_2O_3; and magnet or ferroso-ferric oxide Fe_3O_4; containing respectively, when in pure state, 48·3, 59·9, 70·0, and 72·4 per cent. of metallic iron. But proportions of iron in the rough ores, as actually smelted, much smaller, usually ranging from 25 to 65 per cent. Impure ferrous carbonate one of the most important of English ores. Its occurrence principally in the coal-measures, either in form of earthy masses as clay-iron-stone, or of thin layers as black-band, the latter variety containing from 7 to 15 per cent. and upwards of bituminous combustible matter.

Abundant distribution also of other ferruginous minerals, unimportant in relation to iron-metallurgy, such for example as iron-pyrites FeS_2, one of the chief sources of sulphur; mispickel $FeSAs$, one of the chief sources of arsenic; copper-pyrites $FeCuS_2$, one of the chief sources of copper; chrome-iron-stone $FeCr_2O_4$, the chief source of chromium compounds; and ilmenite $FeTiO_3$, and wolfram $FeWO_4$, the chief sources of titanium and tungsten compounds respectively. Existence also of several well-defined iron phosphates, iron silicates, &c. Further extensive distribution of iron as a minor constituent of very many and very various earths, rocks, and minerals. Its occurrence, moreover, in vegetable and animal kingdoms, especially in the blood of vertebrate animals, so as to constitute 6 or 7 per cent. of the entire ash of their blood.

Metallic iron obtained from the red or black oxide, as found native or produced by calcining the carbonate or hydrate. Either

oxide reducible by carbonous oxide gas, at a very moderate heat, into mass of spongy, difficultly fusible, readily weldable metal (malleable or wrought iron). Property of reduced metal, at a sufficiently high temperature, to combine with carbon and thereby yield a readily fusible compound (cast iron). Property of cast iron, heated in contact with air or iron oxide, to suffer oxidation of its carbon, and so return to the condition of malleable iron. Steel an alloy of iron with carbon, intermediate in composition between cast and malleable iron, procurable from the latter by carburation, and from the former by de-carburation, or oxidation.

Fused malleable iron capable of dissolving up about 5·5 per cent. of carbon, to form an extremely fusible carbide Fe_4C. Solidification of this compound, on sudden cooling, into a uniform, white, hard, brittle, and crystalline mass, completely soluble in hydrochloric acid with evolution of carburetted hydrogen. But by slow cooling of the fused compound, much of its carbon separated, prior to solidification of the metal, in form of minute graphitic scales disseminated through the partially decarburetted iron. Slowly cooled product of a grey colour, and comparatively soft granular texture. Its incomplete solubility in hydrochloric acid to leave a residue of finely divided graphite.

Direct production of malleable iron by heating the purer ores, hæmatite and magnet, on charcoal or coal fires maintained by a blast. Reduced spongy metal collected from time to time upon end of an iron rod. Ball or bloom then strongly heated and welded into a solid mass by hammering. Usual presence in so-produced iron of enough carbon to give it a somewhat steely character (*vide infra*). Its freedom, however, from other impurities, especially if smelted with charcoal. Process primitive and practicable on a small scale; but extravagant in fuel, wasteful in iron, and inapplicable to earthy ores.

Iron usually smelted in large pyriform furnace (blast-furnace) upwards of fifty feet high, and some sixteen feet in maximum diameter at junction of middle with lower third of its height.

Furnace fed from time to time at the top with successive charges of coke or coal, lime or limestone, and calcined or uncalcined ore. Combustion of the fuel maintained by blast of air, constantly forced in through tuyères at the bottom of the furnace. Fuel-carbon burnt in the blast to produce carbonic anhydride with great evolution of heat; and this carbonic anhydride converted, by its consumption of carbon higher up in the furnace, into carbonous oxide with absorption of heat. Reduction of iron oxides effected by so-produced carbonous oxide, with its re-conversion into carbonic anhydride. Gradual descent of resulting infusible spongy iron and its associated earthy matter or clay, with the added lime and unconsumed carbon, to hottest part of the furnace. Combinations effected at this spot of the clay and lime to form a fusible slag, and of the spongy iron with carbon to form a fusible alloy (cast iron) sinking through the slag. Collection of fused products in much constricted lowest portion of furnace, known as the crucible or hearth. Almost continual flowing out of slag through an opening, eight or ten inches above the floor of the crucible. Metal run out every twelve hours or so at lowest point of the crucible, through a tap-hole, kept closed, save at periods of discharge, by a plug of clay.

In working the blast-furnace, air supplied through the tuyères under pressure of three or four pounds on the inch; and, now-a-days, usually at temperature of 300° or so. Substitution of hot for cold blast attended with practicability of using coal instead of coke or charcoal for fuel; and with a great economy, both of fuel in relation to metal yielded, and of yield of metal in relation to ore smelted. But purity and consequent quality of the iron injuriously affected, partly through the high temperature attained and complete exhaustion of the ore effected being favourable to the taking up of impurities; and partly through the not otherwise possible use of more impure materials in the furnace,—of coal instead of less sulphuretted coke, and, in case of 'cinder iron,' of sulphuretted and phosphoretted slags in addition to native ores. General working of hot-blast different

also from that of cold-blast furnace, the intense combustion and consequent high temperature being more localised, and taking place lower down in the furnace.

Presence of 30 to 40 per cent. of combustible constituents, chiefly carbonous oxide, in the gas issuing from mouth of coal-fed hot-blast furnace. Its feeble combustibility when cooled down to the temperature of the air, but ready combustibility at the high temperature at which it leaves the furnace. Issuing gas frequently burnt at mouth of the furnace, with dissipation of $\frac{4}{5}$ of total heat produced (Bunsen and Playfair); but preferably conducted away through wide flues, and used as fuel, both for heating the blast and raising steam wherewith to drive the blast.

Formation of slag, equal in bulk to five or six times the metal yielded, an essential part of iron-smelting operation. Flux most usually employed, limestone or quicklime, to form a fusible compound with the clay of the ore. But with limestone ores an addition of clay, and with quartzose ores an addition of both lime and clay necessary. Hence economical advantage of jointly smelting ores having different varieties of gangue. Composition of ordinary hot-blast slag referrible to formula $Ca_{12}Al_4O_{18}.Si_9O_{18}$, with some lime replaced by magnesia and ferrous and manganous oxides.

Product of cast iron run direct from the blast furnace into rough sand moulds. Resulting pigs of metal distinguished as grey, mottled, and white; and more exactly by numbers from 1 to 8, No. 1 being the darkest grey, No. 8 the whitest white, and the others intermediate. Character of the pig dependent partly on its slow or rapid cooling, as with the carbide Fe_4C (*vide supra*); partly on its composition, as influenced by the working of the furnace and the nature of the ore, flux, and fuel employed. Other conditions being alike, white iron produced with deficit of fuel and appreciable loss of iron in the slag; grey iron with excess of fuel and but little loss of iron in the slag. Pigs of different kinds sometimes furnished by metal from the same tapping.

Grey pig a very valuable form of cast iron, characterised by its grey colour, granular structure, comparative softness so as to admit of being turned on a lathe, comparatively difficult fusibility with dissolution of the separated graphite, and its perfect fluidity when once fused. Proportions of silicon and of total carbon in grey iron usually higher than in other two varieties. Greater part of its carbon left undissolved by hydrochloric acid, in state of graphite. Sp. gr. of grey iron about 7·1. Its chief use for foundry purposes. Act of setting attended with slight expansion; but cooling of the solidified metal with very considerable contraction. In casting to measure, an allowance of one-eighth of an inch to a foot made for shrinking of the metal. Objects usually cast in moulds of sand or loam, but sometimes of iron so as to effect a rapid cooling and consequent whitening and hardening of the external surface of the casting. This process known as 'chilling,' and largely applied to the production of chilled shot for ordnance.

White pig iron of inferior value, save for special purposes. Its uniform brilliant white colour, and hard, brittle, crystalline texture. Its ready fusibility by heat; but its fluidity less perfect than that of grey iron. Its average sp. gr. about 7·5. Its proportions of silicon and total carbon usually less, and of sulphur greater than those of same constituents respectively in other varieties of cast iron. Frequent presence of manganese also to considerably larger extent in white than in darker irons. Curious influence of manganese in preventing the separation of graphite even from very slowly cooled and richly carburetted irons. Complete or almost complete solubility of white iron in strong hydrochloric acid with evolution of carburetted and sulphuretted hydrogen.

Mottled pig a valuable form of cast iron, intermediate between the other two varieties in composition and properties, and superior to both of them in tenacity. But tenacity of cast iron very variable, seldom half that of malleable iron. Superiority, however, of cast iron to malleable iron in its resistance to crushing force.

Cast iron converted into wrought or malleable iron by dis-

charge of its carbon and silicon, through their oxidation by contact either with air or iron oxide at a high temperature. Primitive process of conversion that of 'refining,' still practised in its entirety for production of special qualities of iron; and as the custom of certain localities, more particularly in Germany and Sweden. Principal process of conversion known as 'puddling,' very generally preceded by partial treatment in refining furnace. In case of cast iron, free from sulphur and phosphorus, both methods capable of being superseded by the Bessemer process.

In complete refining process, as practised for the production of the sheet iron used in tin-plate manufacture, some pig iron, usually melted in separate furnace, transferred to a small but somewhat deep quadrangular hearth. Metal covered with charcoal, and played upon by a single blast, with constant stirring about, until sufficiently decarburetted to exchange its fluid state for that of a soft malleable solid. Product collected in a lump at end of an iron bar, subjected to hammering and formed into a slab. Original slab broken into pieces, these welded together, and resulting compound slab passed through the rolling mills.

In ordinary refining process, pig iron placed in a fire-clay-lined iron trough, together with coke or charcoal maintained in combustion by blasts of air supplied through six tuyères, three on each side of the trough, directed obliquely downwards so as to play upon the iron. Consequent fusion and partial oxidation of the metal. After its complete fusion, characteristic appearance of boiling set up, by reaction of interstitial carbon and iron oxide to produce carbonous oxide gas, evolved from the melted metal. After cessation of the boiling, still-fluid metal run out into a flat mould, allowed to set, and suddenly chilled by having water thrown upon it so as to render it capable of easy breaking up. Product known as 'fine-metal.' Slag of refinery furnace, or 'refinery-cinder,' chiefly a silicate of iron $FeO.SiO_2$, re-smelted in blast furnace with fresh ore, to furnish an inferior metal known as 'cinder iron.' Refining process very wasteful of metal; its chief action to effect removal of silicon, in some cases to extent of $\frac{9}{10}$ its original amount; also to effect some reduction

of carbon, and a considerable reduction of sulphur. Proportion of phosphorus, however, scarcely changed.

Refined iron next subjected to puddling; or, not unfrequently, refining process dispensed with altogether, and crude pigs subjected to puddling. Puddling of pig iron attended by a boiling up, similar to that observed in its refining. Process accordingly sometimes spoken of as 'boiling,' the similar treatment of fine-metal being known as 'dry-puddling.' Puddling process conducted by heating the metal in contact with flame on floor of reverberatory furnace, together with oxide of iron (forge scales) and silicate of iron (forge cinder). Fused metal well stirred up with the oxide; and, in case of unrefined iron, complete boiling stage passed through. After considerable removal of carbon, fusibility of the metal proportionately reduced, and its state of perfect fusion replaced by a sandy or dry state with separating out or 'coming to nature' of masses of spongy iron. After complete separation of the spongy iron, temperature of furnace raised by increasing the draught, slag or 'tap-cinder' run off through the floss hole, and the softened metal collected upon end of an iron rod or puddle and rolled and squeezed into rough balls of half a hundredweight or so each. Temperature then further raised, and strongly heated balls placed successively under a steam hammer so as to squeeze out the slag (hammer-slag) and form the iron into coherent masses or blooms. These passed at once through rollers and formed into bars (Puddled or No. 1 bar). Puddled bar cut up into short pieces, the pieces made into bundles, and the bundles, having been strongly heated in furnaces, again passed through the rollers with complete welding together of the fagoted pieces into a compound bar (Merchant or No. 2 bar). Merchant bar doubled on itself, re-heated, and opposed halves welded together by repassing the bar through rollers (Wire Iron or No. 3 bar). Average production of about 88–90 parts of wrought iron from 100 of pig iron by puddling alone; but of not more than 85 parts by joint refining and puddling.

Effect of puddling to reduce the total carbon from 3 or 4 to

as little as $\frac{1}{4}$ per cent., to produce an even greater reduction of the silicon, and to diminish very considerably the small proportions of sulphur and phosphorus originally contained in the pig. Manganese also, when present, very completely discharged by the puddling process. Some further oxidation effected during the welding and rolling. Per-centage results furnished by a particular specimen of cold-blast somewhat grey pig, puddled without previous refining, as follows (Calvert and Johnson):

	Pig Iron.	Puddled Bar.	Wire Iron.
Carbon	2·275	0·296	0·111
Silicon	2·720	0·120	0·088
Phosphorus	0·645	0·139	0·117
Sulphur	0·301	0·134	0·094

In addition to minute proportions of silicon, sulphur, and phosphorus, presence even in best bar iron of some carbon, from 0·1 up to 0·5 per cent. Perfectly decarburetted iron apt to contain oxygen, rendering it white, brittle, and incapable of being welded (burnt iron). Effect of phosphorus in excess to produce 'cold short' iron, brittle at ordinary temperatures. Effect of sulphur in excess to produce 'red short' iron, brittle at a red heat. Wrought iron of good quality characterised by its uniform bluish-white colour, its eminently fibrous texture, and by its ragged torn fracture when broken across.

Steel, an alloy of iron, containing about 1·5 per cent. of carbon; distinguished from pure iron by its property of becoming extremely hard when heated to redness and suddenly cooled; and from cast iron by its tenacity, and its capability of being tempered, or of having its hardness reduced and its elasticity increased by a regulated heating and cooling down. The property of hardening manifested to some extent by ordinary bar iron, in proportion to its amount of carbon. Effect of 0·5 or 0·6 per cent. of carbon to impart a decidedly steely character to the iron. With more than 1·5 per cent. of carbon, steely character of metal lost in that of cast iron. Inferior steels made by oxidising cast iron; best steels by carburetting wrought iron.

Bessemer process. Molten cast iron run into large crucible, or converting vessel, of wrought iron lined with fire-clay; and current of air, under considerable pressure, introduced through tubular openings at the bottom of converting vessel, and blown up through the fluid metal. Process continued for about twenty minutes, attended with great agitation of the metal, and vivid combustion of its carbon and silicon, together with much of its iron, so as to leave a residue of fused wrought iron amounting to 80–85 per cent. of the original cast iron. Resulting metal quite free from silicon, and free to within 0·2 or 0·3 per cent. of carbon, but with fully its original proportions of sulphur and phosphorus. Process consequently limited to best qualities of pig iron, very free from both sulphur and phosphorus. The fused wrought iron converted at once into Bessemer steel by addition to it of requisite proportion of a peculiar white cast iron, known as spiegel-eisen, smelted in Prussia from a spathic ore by means of charcoal. This iron rich both in manganese and carbon, but otherwise singularly pure.

Cementation process. Bar iron of best quality broken up and packed regularly, together with fine charcoal (cement powder), in fire-clay troughs or chests, set in a furnace. The chests, closed with clay or sand, maintained at a full red heat for period of 6 to 10 days, according to quality of steel required, and allowed another 10 days or so to cool down. Bars then found to be covered with blisters, to have exchanged their original fibrous for a finely granular structure, to have become carburetted even to their centres though not uniformly throughout, and to be comparatively easily fusible. The blistered steel then subjected to fagoting and welding, so as to furnish fairly homogeneous bars of metal known as shear-steel. Or the blistered bars melted in fire-clay crucibles and poured into moulds, so as to furnish ingots of cast steel. Improvement in quality of resulting cast steel by fusing the blistered steel with one per cent. of mixed manganic peroxide and charcoal. Cast steel formerly produced only from foreign charcoal-smelted iron; but, now-a-days, since introduction of manganese process, largely from home-made, hot-

blast, coal-smelted iron. Nature of improvement effected, unexplained, not dependent on introduction of manganese into the steel.

Probable nature of cementation process as follows:—Carbonous oxide gas produced by ignition of the charcoal in deficit of air, and freely absorbed by the wrought iron. The absorbed gas subsequently decomposed into carbon retained by the iron and carbonic anhydride discharged through the blisters. This carbonic anhydride, by its contact with the ignited charcoal, reconverted into carbonous oxide, again to be absorbed and decomposed by the iron, and so on:

$$2CO = C + CO_2 \quad \text{and} \quad CO_2 + C = 2CO$$

Sulphur also removed during the cementation, probably as disulphide of carbon.

Natural steel obtained by heating white cast iron in refinery furnace; puddled steel by heating cast iron with iron-oxide in puddling furnace. Processes conducted exactly as for the production of wrought iron, but arrested at an intermediate stage of decarburation. A toughened cast iron, or half-steel, produced by dissolving malleable iron in melted cast iron. Castings requiring considerable tenacity, as stirrups and bits, toughened by heating them in contact with oxide of iron or manganese. Product known as malleable cast iron. Correlatively, forgings requiring considerable hardness converted externally into steely iron by heating them with carbonaceous matters, more particularly with bone dust.

Steel, heated to redness and slowly cooled, very soft; the same steel, heated to redness and suddenly cooled, nearly as hard as diamond. Carbon of soft steel, like that of grey cast iron, partially left as graphite on dissolution of the metal in hydrochloric acid. Carbon of hard steel, like that of white iron, evolved during dissolution of the metal as carburetted hydrogen. Hardest steel exceedingly brittle, and useless for ordinary purposes. Metal tempered, or let down, by heating it to a higher and higher

point indicated by the colour acquired, yellow, brown, purple, blue, and black successively. Colour dependent on formation of a film of oxide of varying thickness, usually, save in the case of watch springs, ground off from the finished articles. Razors and lancets the hardest or least tempered, watch springs and sword blades the softest or most tempered of ordinary steel wares. Cast steel, of good quality, capable of being welded both to steel and to wrought iron. Hence brittleness of hard steel sometimes overcome, especially in the case of cutting instruments, by welding an edge of steel to a tough wrought iron back, and finishing and tempering the compound blade. Capability of being hardened and softened at will, a highly valuable property of steel. Most steel wares, and particularly dies for stamping, wrought in the soft state and afterwards hardened. Presence of some phosphorus in steel used for dies advantageous (Brande). Tenacity of steel double that of malleable iron. Bars of steel and malleable iron of a square inch sectional area, capable of sustaining weights of 50 tons and 25 tons respectively. Sp. gr. of steel 7·6 to 7·8.

Iron scarcely known in the pure state; obtained, by fusing iron wire or filings of bar iron with ferric oxide in a fire-clay crucible, as a lustrous silver-white button, softer than ordinary malleable iron, very tenacious, and of sp. gr. 7·844. Iron also producible, in pulverulent state, by heating ferric oxide in current of hydrogen; in crystals belonging to the regular system, by heating ferrous chloride in current of hydrogen; and as flexible laminæ, by electrolysing solution of double ferrous and ammonium chloride. Sp. gr. of electrolytic iron 8·14. Its incapability of being hardened by sudden cooling, and its dissolution in dilute acids with evolution of odourless hydrogen.

Iron, in its purest commercial form, a highly lustrous greyish-white metal, of fibrous texture, considerable hardness, and sp. gr. 7·7. Its ductility very great; its tenacity far superior to that of other metals (nickel and cobalt alone excepted), and nearly double that of copper, the next most tenacious of the metals in common use. Malleability of iron at ordinary temperatures inconsiderable. Its characteristic softening at a red heat and up-

wards. Its capability of being welded at a full red or incipient white heat. Its fusion only at strongest heat of a wind furnace.

Iron an inferior conductor of heat and electricity. Its susceptibility to magnetic induction altogether peculiar in degree, and far exceeding that of the next most susceptible metals, nickel and cobalt. Pure iron, however, incapable of permanent magnetisation. This property limited to certain of its compounds with carbon, oxygen, and sulphur, or steel, loadstone, and magnetic pyrites respectively. Temporary loss of magnetic susceptibility by iron at a red heat.

Iron especially rendered valuable for various purposes by its great strength and rigidity; its comparatively low specific gravity; its difficult fusibility; and its ready capability of being softened by heat, forged, and welded. Also by its property of uniting with carbon to form steel and cast iron, the one alloy characterised by its hardness, elasticity, and strength, the other by its fusibility, and both by their susceptibility to diverse modifications in physical character fitting them for diverse applications.

Iron at a red heat, capable experimentally of absorbing four times its volume (measured cold) of carbonous oxide gas, and one-half its volume of hydrogen. Both gases given off unchanged on heating the metal in vacuo. Presence in all forged iron of eight or ten times its volume of carbonous oxide, and in meteoric iron of two or three times its volume of hydrogen.

Variable chemical susceptibility of iron according to its physical condition. Metal in pulverulent state, as obtained by reducing precipitated ferric oxide at a low temperature with hydrogen or carbonous oxide, pyrophoric. Compact iron indifferent to dry air, at ordinary temperatures. Its acquirement of a film of oxide at 250° and upwards. Its combustibility in air at a red or white heat, according to its state of division; and brilliant combustion in oxygen, even when heated but to dull redness. Combustion attended with vivid scintillation but not with flame.

In absence of air, iron in massive state quite unaffected by

contact with water. Metal also preservable unchanged in solutions of soda, potash, lime, baryta, and of carbonated but not super-carbonated alkali. Characteristic rusting of iron when immersed in fresh or salt water open to the air, or when exposed jointly to air and moisture. Rusting of massive iron a comparatively slow operation. Process set up in points; and continued by a voltaic action, with iron for the oxidisable, rust for the negative element (?). Alleged influence of atmospheric carbonic acid in promoting the process. Rusting of more or less divided iron very rapid. Temperature quickly raised, from 15° to 40° or 50°, by the rusting of half a hundredweight of coarse iron borings wetted with water. Presence in resulting rust of a considerable proportion of ferrous oxide. Oxidation of finely ground iron-powder wetted with water instantaneous, accompanied by great manifestation of heat, formation of the magnetic oxide, and a sensible evolution of hydrogen. Constant presence in iron rust of more or less ammonia, derived probably from action of nascent hydrogen on nitrogen of the atmosphere, possibly from an absorption of atmospheric ammonia. Ready decomposition of steam by fully ignited iron, with liberation of hydrogen and formation of magnetic iron oxide partly in crystalline state:

$$4H_2O \quad + \quad Fe_3 \quad = \quad 4H_2 \quad + \quad Fe_3O_4$$

Iron rapidly attacked by chlorine, bromine, and iodine, both in dry state and in aqueous solution. Its indifference to sulphur up to a dull red heat, but combination therewith at higher temperatures to form ferrous sulphide. Violent reaction after some time of moistened mixture of sulphur and iron-filings, frequently attended with combustion. Direct combination of iron at a red heat with phosphorus, arsenic, silicon, and carbon.

Iron attackable by aqueous acids, even when of the feeblest character and in much diluted state. Its solution in aqueous carbonic acid for instance; with liberation, under exclusion from air, of hydrogen gas, and formation of ferrous carbonate dissolved in the excess of carbonic acid water. Iron also attacked, with liberation of hydrogen, when heated with the fatty acids and

water under pressure. Its ready dissolution in hydrochloric and dilute sulphuric acids with copious evolution of hydrogen. Its reaction, however, with strong and even boiling sulphuric acid, to furnish sulphurous anhydride, very inconsiderable. Iron attackable by even the weakest nitric acid, and rapidly dissolved by acid of 1·1 to 1·4 specific gravity, with evolution of nitric oxide, &c. But clean iron apparently quite unaffected by immersion even for years in colourless acid of sp. gr. 1·45 and upwards. Iron dipped for a longer or shorter time in acid of this strength and then in weaker acid, quite unaffected by the weaker acid if of sp. gr. 1·35, but immediately acted upon by an acid of yet inferior gravity. Iron, unattackable by acid of sp. gr. 1·35 to 1·45, said to be in passive state. Its condition attributed to formation on its surface of a film of ferric oxide, soluble only in more dilute acid. Iron rendered passive not only by its immersion in nitric acid of sp. gr. 1·45 and upwards, but also by heating it in a gas- or spirit-flame for a few seconds; or by immersing it in acid of sp. gr. 1·35, and, even while rapidly dissolving, touching it under the liquid with a piece of platinum, plumbago, &c., so as to make it a zinc-electrode. Iron acting as the zinc-ode of a battery, or what comes to the same thing, while in electric contact with a piece of immersed platinum, or even of immersed passive iron, quite unaffected by immersion in nitric acid of sp. gr. 1·35. Attackability of passive iron at once restored by making it the platinode, as by touching it while immersed in the acid with a piece of dissolving zinc, iron, &c. Also by exposing it to the air for a few seconds, or wiping it with a cloth.

Iron little attacked by fused caustic alkali; but, especially when in form of filings, readily oxidised by fused nitre, with production of some ferrate of potassium. Rusting of iron in air promoted by presence of ammoniacal vapours.

Chemical reactions of cast iron and steel for the most part similar to those of malleable iron. Grey cast iron less readily oxidisable, and steel and white cast iron much less readily oxidisable by exposure, than malleable iron. But coloration, and further oxidation by heat, more facile with white iron and steel

than with malleable iron. Complete dissolution of white iron and steel in concentrated muriatic acid, with evolution of offensively smelling carburetted hydrogen; and, in case of the white iron, with separation of a liquid petroleum-like compound. Some carburetted hydrogen also formed during solution of grey iron in the concentrated acid; but considerable residue of graphite left undissolved. White iron and even steel but slowly attacked by dilute muriatic acid. Characteristic blackening of both alloys when touched with nitric acid. Grain of steel, dependent on unequal carburation, brought out by washing its surface with dilute nitric acid. Result seen in damasked sword-blades, &c. Steel, like iron, capable of assuming the passive state by immersion in strong nitric acid, &c. Slow action of very dilute acids, and of saline solutions as sea-water, on steel and cast iron, to leave a bulky, soft, black residue, having the form of the original mass, and consisting mainly of a readily combustible, feebly magnetic carbide of iron.

Iron-alloys proper, of but little importance. In tinned-iron and zinked-iron the constituent metals held together by true intermediate alloys. Iron capable of alloying more or less freely with aluminium, tin, manganese, nickel, platinum, rhodium, iridium, &c., and of taking up minute but variable proportions of nearly all metals whatsoever.

Derivation from iron of a series of diad or ferrous compounds, typified by ferrous oxide FeO, and chloride $FeCl_2$, the analogues of zinc oxide and chloride, ZnO and $ZnCl_2$ respectively; of a series of triad or quasi-triad or ferric compounds, typified by ferric oxide Fe_2O_3, and chloride Fe_2Cl_6 or $FeCl_3$, the analogues of aluminic oxide and chloride, Al_2O_3 and Al_2Cl_6 or $AlCl_3$ respectively; of a few intermediate ferroso-ferric compounds, typified by magnet $FeO.Fe_2O_3$, the analogue of franklinite $ZnO.Fe_2O_3$, gahnite $ZnO.Al_2O_3$, &c.; and of a few yet higher compounds, more especially pyrites FeS_2, the analogue of carbonic sulphide CS_2; and potassium ferrate $K_2O.FeO_3$ or K_2FeO_4, the analogue of potassium sulphate K_2SO_4, chromate K_2CrO_4, &c.

FERROUS SALTS.

Chloride, $FeCl_2$; obtained in anhydrous state, as a sublimate of yellowish-white scales, by passing hydrochloric acid or chlorine over excess of iron turnings heated to redness. Compound also obtained by desiccation of the hydrate, at a moderate heat, out of access of air. Ferrous chloride fusible at a red heat and volatile at a higher temperature. Its reactions, when heated in dry air, to furnish ferric oxide and ferric chloride; and, when heated in current of steam, to furnish ferroso-ferric oxide, hydrochloric acid, and hydrogen:

$$6FeCl_2 + O_3 = Fe_2O_3 + 2Fe_2Cl_6$$

$$3FeCl_2 + 4H_2O = Fe_3O_4 + 6HCl + H_2$$

Its reduction by hydrogen, at a gentle heat, to yield pure iron crystallised in cubes. The hydrate $FeCl_2.4Aq$, easily obtained by dissolving iron in aqueous hydrochloric acid, filtering liquid at boiling heat before complete solution of the metal or saturation of the acid, and cooling the filtrate in closed vessels. Deposition of deliquescent bluish-green prismatic crystals, gradually oxidising on exposure to air. Combination of ferrous chloride with alkali chlorides to form crystallisable double salts, as $2KCl.FeCl_2.2Aq$, and $2NH_4Cl.FeCl_2.2Aq$.

Iodide, FeI_2; made by digesting excess of iron with iodine in gently heated water, and evaporating out of contact with air. Obtainable, in hydrated state, as green deliquescent needles; in anhydrous state, as a grey, metal-lustrous, crystalline mass; in either state decomposible on exposure to air, with oxidation of its iron and separation of iodine.

Oxide, FeO; a scarcely known compound, best made by igniting the oxalate at a low temperature out of access of air. The hydrate $FeO.H_2O$ (?), thrown down as a gelatinous, almost white precipitate, on addition of pure ferrous chloride or sulphate to excess of dilute air-free caustic alkali in the cold. Its rapid absorption of atmospheric oxygen, with acquisition of a green,

and finally of a red colour. Its apparent dehydration at a boiling heat, with considerable darkening in colour. Sparing solubility of precipitated ferrous hydrate in aqueous ammonia and sal-ammoniac.

Sulphide, FeS; made in anhydrous state by direct combination of sulphur with fully ignited massive iron; or by heating together a mixture of sulphur and iron-filings. Semi-metallic, crystalline, fusible mass, dissolving in dilute mineral acids with evolution of sulphuretted hydrogen. Compound precipitated in hydrated state, by action of soluble sulphides and sulphydrates upon ferrous salts, as a black velvety precipitate readily soluble in acids, and quickly oxidising on exposure to air, chiefly into hydrated ferric oxide and sulphur, partly into ferrous sulphate. Formation of a sub-sulphide of iron Fe_2S, by ignition of ferrous sulphate in a current of hydrogen.

Nitrate, $Fe(NO_3)_2$. Dissolution of iron in dilute nitric acid accompanied with formation of nitrate of ammonia; in stronger acid, with formation of ferric nitrate. Pure ferrous nitrate obtainable by decomposing ferrous sulphate with nitrate of barium; and, together with sulphuretted hydrogen, by dissolving ferrous sulphide in cold dilute nitric acid. Its production, on evaporation of solution in vacuo, in pale-green hydrated crystals $Fe(NO_3)_2.6Aq$. Its decomposition by a gentle heat, or on keeping, with evolution of nitric oxide, and formation of basic ferric nitrate:

$$2H_2O \quad + \quad 3Fe(NO_3)_2 \quad = \quad NO \quad + \quad Fe_3\begin{cases}(NO_3)_5\\(HO)_4\end{cases}$$

Carbonate, $FeCO_3$; found native in yellowish-brown crystals, usually as iron-spar isomorphous with talc-spar, rarely as junckerite isomorphous with arragonite. Its abundant occurrence also in admixture with clay and bituminous shale, as clay-ironstone and black-band iron-stone respectively. Ferrous carbonate converted by calcining or roasting into the peroxide, and by ignition in close vessels into the magnetic oxide:

$$3FeCO_3 \quad = \quad Fe_3O_4 \quad + \quad 2CO_2 \quad + \quad CO$$

The hydrated carbonate thrown down, as an almost white precipitate, by the action of alkali carbonates on ferrous salts. Its speedy conversion into hydrated ferric oxide by exposure to air, with assumption of an intermediate green and final ochrey-red colour. Slight solubility of precipitated ferrous carbonate in carbonic acid water. Occurrence of similarly dissolved ferrous carbonate in chalybeate springs; furnishing ochrey deposit of ferric hydrate on their exposure to air:

$$4(FeO.CO_2) + O_2 + 3H_2O = 2Fe_2O_3.3H_2O + 4CO_2$$

Sulphate, $FeSO_4$; known in hydrated state as green vitriol or copperas; produced on commercial scale by weathering of pyrites, exhaustion of the product with water, and evaporation of the solution. Also made by dissolving metallic iron or ferrous sulphide in dilute sulphuric acid at a gentle heat. Deposition from cooled filtrate of bluish-green clino-rhombic prisms, with 7 molecules of water. Ferrous sulphate also producible crystallised with 5, 4, 3, and 2 molecules of water; the tetrahydrated salt, isomorphous with ordinary manganous sulphate, by crystallising the aqueous solution at 80°; and the dihydrated salt, isomorphous with gypsum, by dissolving the ordinary salt in oil of vitriol, and setting aside. The monohydrate left as a white powder by heating the ordinary salt to 115°. Its unalterability by further heating up to 280°. Production at higher temperatures, though with difficulty, of the anhydrous compound decomposible at a red heat:

$$2FeSO_4 = Fe_2O_3 + SO_3 + SO_2$$

Distillation, at a red heat, of the partially dried and oxidised salt to furnish Nordhausen acid $H_2SO_4.SO_3$, and leave residue of ferric oxide, known as colcothar.

Slow efflorescence of crystallised green vitriol; and oxidation of the effloresced salt on exposure to air, to yield ochrey pseudomorphous masses of basic ferric sulphate. Free solubility of green vitriol in water; its insolubility in alcohol, and precipitation by alcohol from state of aqueous solution, as a green crystalline

powder scarcely oxidisable on exposure to air. The aqueous solution quickly oxidised on exposure, with production of normal ferric sulphate in solution, and a hydrated basic salt precipitated:

$$4(FeO.SO_3) \quad + \quad O_2 \quad = \quad Fe_2O_3.3SO_3 \quad + \quad Fe_2O_3.SO_3$$

Absorption of oxygen by ferrous sulphate, not only from the atmosphere, but from various reducible compounds, whence its very general employment as a reducing agent—to effect the reduction of nitric and hypochlorous acids, and of mercuric and auric salts for instance.

Absorption by ferrous sulphate, as by other dissolved ferrous salts, of nitric oxide gas, to form a dark-brown solution of the compound $2FeSO_4.NO$; decomposible, by ebullition out of contact with air, into ferrous sulphate and nitric oxide, by oxidation through exposure to air, into mixed ferric sulphate and nitrate. Combination of ferrous sulphate with sulphates of potassium and ammonium, &c., to form crystallisable hexahydrated double salts, as $K_2Fe(SO_4)_2.6Aq$, isomorphous with potassio-magnesium sulphate, &c.

Phosphate. Production, on adding ferrous sulphate to sodium phosphate solution, of a white precipitate, becoming bluish by oxidation. The compound $Fe_3(PO_4)_2.8Aq$, found native as vivianite.

FERRIC COMPOUNDS.

Chloride, $FeCl_3$ or Fe_2Cl_6; produced, in anhydrous state, by passing chlorine gas over gently heated iron or ferrous chloride. Also by heating the residue left on evaporating the aqueous solution to dryness. A sublimate of black iridescent scales, volatilising at a little above 100°. Its vapour-density $162{\cdot}5 = \frac{112 + 213}{2}$, corresponding to the molecule Fe_2Cl_6. Its deliquescence, and solubility in water with hissing noise to form the hydrated salt. Its decomposition when heated in air to liberate chlorine, and when heated in steam to liberate hydro-

chloric acid, leaving in both cases a residue of ferric oxide. The hydrated salt produced by dissolving ferric oxide or hydrate in hydrochloric acid and evaporating down; or by dissolving metallic iron in hydrochloric acid and chlorinating the product, by acting on it with chlorine gas or with a mixture of hydrochloric and nitric acids:

$$6FeCl_2 + 6HCl + 2HNO_3 = 3Fe_2Cl_6 + 4H_2O + 2NO$$

Hydrated ferric chloride usually met with as a red-brown or yellow-brown solution, the latter containing excess of acid, or probably the double salt $2HCl.FeCl_3$. By evaporating a not too acid solution, the hydrated chloride $FeCl_3.3Aq$, deposited in large orange-red deliquescent crystals. Solution of ferric chloride decomposed by evaporation to dryness with evolution of hydrochloric acid, and production of an indefinite oxichloride, decomposible by heat into residuary ferric oxide and volatilised ferric chloride. Solubility of recently precipitated ferric hydrate to a considerable extent in neutral ferric chloride solution. Existence also of various insoluble hydrated oxichlorides, producible by exposing ferrous chloride solution to the air and in other ways. Occasional employment of ferric chloride as an oxidising agent. Its reduction to state of ferrous salt by sulphurous acid, sulphydric acid, &c.:

$$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S$$

Its combination with alkali chlorides to form the crystallisable double salts $2KCl.FeCl_3.Aq$, $2NH_4Cl.FeCl_3.Aq$, &c. Considerable solubility of ferric chloride both in alcohol and ether.

Hydrates. Combinations of ferric oxide with water to form hydrates of different character and composition. The normal hydrate $3H_2O.Fe_2O_3$, unknown with certainty; said to constitute one variety of bog-iron-ore; probably produced as the gelatinous red-brown precipitate thrown down from cold dilute ferric chloride solution by excess of ammonia. The di-hydrate

$2H_2O.Fe_2O_3$, found native, in fibrous crystals or masses, as xanthosiderite. The sesqui-hydrate $3H_2O.2Fe_2O_3$, the most common of ferric hydrates, found native as brown hæmatite or limonite; produced by exposing precipitated ferrous hydrate or carbonate to the air, and by the rusting of metallic iron. The mono-hydrate $H_2O.Fe_2O_3$, found native in crystalline state as göthite or needle-ore; produced by desiccation of precipitated ferric hydrate at 120°; and by decomposing the compounds $Na_2O.Fe_2O_3$ and $K_2O.Fe_2O_3$ with boiling water. Existence of different ferric hydrates, in impure state, as red and yellow marl, ochre, umber, &c. Native ferric hydrate usually of a yellow-brown colour. Appearance of the artificial product very variable. Its texture pulverulent, loose, and even velvety; its colour an almost bright yellow, an almost bright though dark red, and nearly every shade of brown, according to circumstances. The crystalline and some amorphous varieties of the native hydrate unattackable by weak acids as the sulphydric and acetic, and difficultly soluble even in strong hydrochloric acid at a boiling heat. But the amorphous hydrates, native and artificial, for the most part readily blackened by sulphydric acid, and dissolved by acetic and dilute hydrochloric acids. Ferric hydrate largely used in gas-purification to absorb sulphuretted hydrogen. Resulting ferrous sulphide reconverted into ferric hydrate by exposure to air, and entire process repeated indefinitely:

$$Fe_2O_3.xAq + 3H_2S = 2FeS.xAq + S + 3H_2O$$
$$2FeS.xAq + O_3 = Fe_2O_3.xAq + S_2$$

Ferric hydrate easily reducible by contact with decaying organic bodies, and the resulting ferrous compound easily re-oxidisable by exposure to air, whence the effect of ferric hydrate in promoting decay or eremacausis. Action of ferric hydrate as a mordant by its combination with both vegetable fibre and colouring matter. Dehydration of ferric hydrate by gentle ignition, by prolonged heating in a mercury bath, and by ebullition with a saturated solution of calcium chloride, &c.

A curious variety of ferric hydrate obtained by boiling the washed precipitated hydrate for 8 or 10 hours in water. Its insolubility in strong hydrochloric acid; but dissolution in dilute hydrochloric and acetic acids to form non-astringent red solutions, turbid by transmitted light, precipitable by strong hydrochloric acid and alkali-metal salts, not yielding prussian-blue on addition of ferrocyanide of potassium. Ferric hydrate producible in state of aqueous solution by dialysis of its ferric chloride solution. Gelatinisation of resulting red liquid, spontaneously after some weeks, or immediately on addition of alkali-metal salts, &c.

Oxide, Fe_2O_3. Abundant existence of crystalline ferric oxide as oligiste or specular iron, especially in island of Elba. Its occurrence in rhombohedrons approximating closely to cubes (and as martite, in regular octahedrons), of sp. gr. 5·2, having a metallic, iridescent, black colour, and yielding a red powder. Abundant existence also of amorphous ferric oxide as red hæmatite, in hard, fibrous, mammillated, dull-red masses, of sp. gr. 5·0. Crystalline ferric oxide produced artificially, in form of dense reddish-tinted black scales, by igniting ferrous sulphate in admixture with sulphate or chloride of sodium, and in other ways. Its production in amorphous state as a brown-red powder, by gently heating ferric hydrate, ferrous carbonate, ferrous oxalate, &c.; or by strongly igniting ferrous sulphate.

Ferric oxide usually non-magnetic. Its hardness about that of apatite or felspar. The artificial amorphous oxide, especially that obtained by ignition of ferrous sulphate, largely used under the name of colcothar, or rouge, for polishing plate and glass. A compact form of red-hæmatite, known as blood-stone, also much used for polishing metal trinkets, &c.

Ignition of the ferric oxide, obtained by heating the precipitated hydrate to 350°–450°, attended with incandescent glow and considerable shrinking. Reduction of the oxide to state of ferroso-ferric oxide, with evolution of oxygen, by intense ignition. Its ready reduction to metallic state by hydrogen or carbonous oxide at a heat short of redness. Its action in promoting the incineration of organic substances, by giving up its oxygen

to the combustible and re-absorbing oxygen from the air. Its reaction with sulphur at a gentle heat to form sulphurous anhydride and ferrous sulphide, the latter reconverted into ferric oxide when heated in current of air. Expulsion of carbanhydride from fused alkali carbonates by ferric oxide, to form the compounds $K_2O.Fe_2O_3$, $Na_2O.Fe_2O_3$, &c., decomposible by water to leave the monohydrate $H_2O.Fe_2O_3$. Its oxidation by fused nitre to form ferrate of potassium $K_2O.FeO_3$ or K_2FeO_4. Solubility of ferric oxide in mineral acids, especially hydrochloric acid, to form ferric salts,—with considerable difficulty, however, in the case of red-hæmatite and of the strongly ignited artificial amorphous oxide.

Ferroso-ferric oxide, Fe_3O_4. Combination of ferric oxide as an anhydride with different monoxides, to form definite compounds analogous to the monohydrate $H_2O.Fe_2O_3$, &c. The zinc compound $ZnO.Fe_2O_3$, found native as franklinite; and the ferrous compound $FeO.Fe_2O_3$, as magnet or loadstone. Crystallisation of both minerals, and of their analogues $ZnO.Al_2O_3$, or gahnite, $MgO.Al_2O_3$ or spinelle, $FeO.Cr_2O_3$ or chrome-iron, &c., in forms of the regular system, chiefly octahedral. Magnet the richest of iron ores. Its abundant occurrence, in Sweden and parts of North America, in form of hard, black, metal-lustrous, crystalline masses, of sp. gr. 5·0, fusible at a full red heat. Compound producible artificially in form of forge-scales; also by combustion of iron in oxygen; by its ignition in current of steam; by ignition of ferrous carbonate out of access of air; by strong ignition of ferric oxide; and in other ways. Magnetic iron oxide producible also in the hydrated state as $H_2O.Fe_3O_4$ or $\left.\begin{matrix}H_2O\\FeO\end{matrix}\right\}Fe_2O_3$, by direct combination of precipitated ferrous and ferric hydrates. Compound best made by precipitating mixed solutions of ferrous and ferric salt with excess of ammonia at a boiling heat; but also producible by precipitating the two solutions separately in the cold, and boiling the resulting gelatinous magmas, pale green and brown-red respectively, with one another. In either way, the magnetic oxide formed as a dense, quickly subsiding, dead-black precipitate, but very slowly

oxidisable. The magnetic hydrate also formed by boiling precipitated ferric hydrate with excess of iron turnings, the reaction being attended with some evolution of hydrogen:

$$Fe + H_2O + Fe_2O_3.Aq = H_2 + FeO.Fe_2O_3.Aq$$

The anhydrous and hydrated compound alike strongly magnetic, and soluble in hydrochloric acid to form a mixture of ferrous and ferric chlorides.

Sulphides. Ferric sulphide Fe_2S_3, scarcely known as a definite compound; said to constitute the black precipitate formed by adding ferric chloride or sulphate, drop by drop, to excess of alkali sulphide or sulphydrate solution. Also considered to exist combined with ferrous sulphide in magnetic pyrites $FeS.Fe_2S_3$ or Fe_3S_4, and combined with cuprous sulphide in copper pyrites $Cu_2S.Fe_2S_3$ or $Cu_2Fe_2S_4$. Magnetic pyrites found native in bronze-yellow, metal-lustrous, tabular crystals, of sp. gr. 4·5, belonging to the rhombohedral system. Compound attracted, though not very strongly, by the magnet, and sometimes itself magnetic. Its weathering on exposure to air, unalterability by ignition in close vessels, and solubility in dilute hydrochloric acid with evolution of sulphuretted hydrogen and separation of sulphur. Composition of different specimens of magnetic pyrites variable between Fe_3S_4 and Fe_7S_8. Product obtained by heating ferrous sulphide FeS, with excess of sulphur, and by igniting pyrites FeS_2, in close vessels, usually referred to the latter formula.

Ferric persulphide, or iron pyrites FeS_2, apparently the analogue of manganic peroxide MnO_2. Its unimportant production artificially, by exposing mixed ferrous sulphide and sulphur to heat below redness. Its occurrence native in two principal forms; as yellow pyrites, or mundic, crystallised in the regular system, usually in cubes; and as white pyrites, or marcasite, in orthorhombic prisms and reniform radiated masses. Sp. gr. of yellow pyrites about 5·0; of white pyrites about 4·7. Both varieties found in rocks of all ages; but yellow pyrites most abundantly in the older strata. Yellow pyrites in compact state

but little affected by exposure to air. White pyrites quickly disintegrated, with formation of ferrous sulphate. Both varieties unaffected by the magnet, converted into the magnetic sulphide by ignition in close vessels, combustible in air to yield ferric oxide and sulphurous anhydride, and insoluble in dilute hydrochloric or sulphuric acid. Combustion of yellow pyrites conducted on large scale for sake of the produced sulphurous anhydride, afterwards converted into sulphuric acid. Arsenical pyrites or mispickel, FeAsS, a tolerably abundant mineral, crystallising isomorphously with marcasite, and having much the same general appearance. Its sp. gr., however, 6·8. Its decomposition when heated in close vessels to evolve metallic arsenic, and when heated in air to evolve arsenious and sulphurous anhydrides.

Sulphate, $Fe_2(SO_4)_3$; found native, with 9 atoms of water, as the mineral coquimbite, in fine-grained pulverulent masses, and crystallised in hexagonal prisms. Producible by dissolving ferric oxide or hydrate in sulphuric acid; usually made by adding one proportion of sulphuric acid to two proportions of green vitriol, and oxidising the mixture with nitric acid:

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 4H_2O + 2NO$$

Production, on evaporation, of a brown-tinted white, fibrous, deliquescent mass, dissolving in water to form yellow-brown liquid, affording the usual reactions of a dissolved ferric salt. Deposition, on mixing a slightly acid solution of ferric sulphate with sulphate of ammonium and setting aside, of ammonia-iron-alum $(NH_4)Fe(SO_4)_2.12Aq$, in almost colourless, sometimes brownish or amethystine, octahedral crystals. The potassium salt $KFe(SO_4)_2.12Aq$, producible in a similar manner, but somewhat unstable both in solid state and in solution. Existence of numerous basic ferric sulphates, formed by aërial oxidation of green vitriol solution under different circumstances, and in other ways. The salt $Fe_2(SO_4)_3.Fe_2O_3.18Aq$, found native in capillary crystals as fibro-ferrite; and the salt $2Fe_2(SO_4)_3.Fe_2O_3.3Aq, = 6Fe(SO_4)(HO)$, as fibrous coquimbite.

Phosphates. The hydrate $FePO_4.2Aq$, thrown down as a

white precipitate by addition of ferric chloride or acetate to sodium phosphate solution. Its insolubility in acetic acid; solubility in excess of ferric chloride or acetate. The basic salts $Fe_2PO_4(HO)_3$, and $Fe_2PO_4(HO)_3.9Aq$, found native as green-ironstone and delvauxite respectively. The hydrated arseniate $FeAsO_4.2Aq$, producible as a white precipitate, and found native as scorodite.

Ferrates. The potassium salt K_2FeO_4 or $K_2O.FeO_3$, produced as a friable mass, by projecting a mixture of nitre and iron filings into a capacious crucible kept at a dull red heat; also by heating to redness for some time a mixture of nitre and ferric oxide. Salt obtainable in the wet way by passing current of chlorine gas through hydrated ferric oxide suspended in very strong potash. Eventual deposition of produced potassium ferrate, from its insolubility in the strong alkali, as a black powder afterwards drained on a tile. Solubility of potassium ferrate in water to form a deep crimson solution, preservable for some time when in concentrated state, but quickly decomposing on dilution, even in the cold, with evolution of oxygen and precipitation of ferric hydrate. Solution producible only with alkali in excess. Its incapability of neutralisation; and immediate decoloration by oxidisable bodies. Ferrate of barium procurable from the potassium salt by double decomposition, as a rose-red precipitate of considerable stability.

Ferrous compounds recognisable by giving to the borax bead, heated in the reducing frame, a bottle-green colour; ferric compounds, by giving to the bead, heated in the oxidising flame, a yellow-brown colour. Both sets of compounds reducible by ignition with carbonate of sodium on charcoal, to leave an unfused metallic residue attracted by the magnet.

Solutions of both sets of compounds decomposed by sulphide of ammonium to yield a black precipitate of iron sulphide, readily soluble (in case of ferric salt, with some deposit of sulphur) in diluted acids. Also by caustic alkalis to yield the hydrated oxides, greenish and ochrey-red respectively, both of them inso-

luble in excess of fixed alkali, but the green ferrous precipitate somewhat soluble in excess of ammonia and sal-ammoniac.

Ferrous best distinguished from, and recognised in presence of, yellow ferric solutions by giving a deep-blue precipitate with ferridcyanide of potassium. Ferric best distinguished from, and recognised in presence of, green ferrous solutions, by giving a blue precipitate with ferrocyanide, and a deep red colour with sulphocyanide of potassium.

Ferrous converted into ferric solutions by action of chlorine water or alkali hypochlorite in the cold, or of nitric acid at a gentle heat. Ferric solutions, preferably much diluted, reduced to state of ferrous solutions by treatment with sulphurous acid; or by prolonged action of sulphuretted hydrogen, with correlative deposition of sulphur; or by means of nascent hydrogen, furnished by dissolution of pure metallic zinc in acid.

In common with aluminic and chromic solutions, but unlike solutions of ordinary diad metals, solutions of ferric salts precipitated, and that completely, by digestion with the carbonates of calcium, strontium, and barium. Further, with ferric and cobaltous or manganous &c. salts in solution together, the ferric salt, with care, completely precipitable by addition of caustic or carbonated alkali and ebullition, prior to any of the cobaltous or manganous salt being precipitated. Nearly neutral solutions of ferric salts also completely precipitated by addition of alkali succinate or benzoate, and by ebullition with alkali acetate.

(91.) Cobalt.

Cobalt, as regards its sources and extraction, conveniently considered in connection with closely allied metal, nickel. Correlation of the two metals by a remarkable similarity of properties and behaviour. Their differentiation chiefly through greater tendency of cobalt to become peroxidised and to yield characteristic peroxidised or corresponding compounds.

Cobalt not an abundant element. Its principal sources smaltine or tin-white cobalt $CoAs_2$, and cobaltine or cobalt glance $CoAsS$.

Its occurrence also as an arseniate, as a sulphate, as a peroxide in admixture with manganic peroxide, &c. Native metallic cobalt found only in meteorites, to amount of 0·1 to 1·0 per cent.

Nickel more abundant than cobalt; found chiefly as kupfer-nickel, but also met with in many different forms, such as cloanthite $NiAs_2$, nickel glance NiAsS, &c. &c. Principal sources of nickel, kupfer-nickel NiAs or Ni_2As_2, and another arsenide Ni_3As_2, produced artificially in smalt manufacture, and known as speiss. Occurrence of metallic nickel in meteoric iron, to amount ranging usually from 4 or 5 to 10 per cent.

Nickel and cobalt ores usually very complex. The two metals found in almost invariable admixture to greater or less extent with each other, and with copper and iron. Arsenic of the several ores further replaced habitually by more or less antimony and bismuth.

Details of treatment of nickel and cobalt ores, including speiss, very various. The ore usually roasted in current of air, so as to drive off much of its arsenic and oxidise the remainder. Roasted ore then dissolved in hydrochloric acid, and arsenic of resulting solution precipitated, either as sulphide together with sulphides of antimony, bismuth, copper, &c.; or, more usually, together with iron as ferric arseniate, so as to avoid the prolonged treatment with sulphuretted hydrogen otherwise required. In former case, the solution filtered off from precipitated sulphides, boiled to expel sulphuretted hydrogen, oxidised with nitric acid and precipitated with carbonate of sodium. The washed precipitate, consisting of peroxide of iron and basic carbonates of nickel and cobalt, digested with excess of aqueous oxalic acid, and resulting soluble ferric oxalate removed by washing from the insoluble oxalates of nickel and cobalt. These oxalates then dissolved in ammonia, and their solution exposed to air. Consequent gradual deposition of nickel oxalate, the cobalt remaining in solution as an ammoniacal cobaltic compound. Or the solution, after action of sulphuretted hydrogen and oxidation by nitric acid, treated with excess of ammonia so as to precipitate ferric oxide and leave cobalt and nickel in solution. Ammoniacal

solution then exposed to air, and hydrated nickel oxide precipitated therefrom by addition of caustic potash, the cobalt remaining in solution as an ammoniacal cobaltic compound. Cobalt obtainable in form of oxide, from either ammoniacal cobaltic solution, by evaporating to dryness and igniting the residue.

In latter case, hydrochloric acid solution of the roasted ore oxidised with bleaching powder or nitric acid, and then nearly neutralised with milk of lime or carbonate of sodium at boiling heat so as to effect the precipitation of ferric arseniate. With deficit of iron in the ore, a soluble ferric salt sometimes added; and, anyhow, by cautious addition of the precipitant, the whole both of the arsenic and iron precipitated. Solution next treated with sulphuretted hydrogen to precipitate bismuth, copper, &c., leaving nickel and cobalt in solution. Cobalt then precipitated as peroxide by solution of bleaching powder, avoiding neutralisation of the mixed liquid; and nickel afterwards thrown down as oxide by milk of lime. Or the nickel and cobalt precipitated together as carbonates, the washed carbonates suspended in water, and a current of chlorine gas passed through the liquid. Cobalt thereby left in state of undissolved peroxide; nickel in state of dissolved nickel chloride, precipitable by lime or carbonated alkali:

$$2(CoO.CO_2) + NiO.CO_2 + Cl_2 = Co_2O_3 + NiCl_2 + 3CO_2$$

And with each metal respectively in excess:

$$2(CoO.CO_2) + H_2O \quad Cl_2 = Co_2O_3 + 2HCl + 2CO_2$$

$$H_2O + NiO.CO_2 \quad Cl_4 = 2HClO + NiCl_2 + CO_2$$

Other methods of separating cobalt from nickel based on conversion of the former metal into insoluble cobalt-yellow by nitrite of potassium; into soluble cobalto-cyanide of potassium by cyanide of potassium, &c.

Cobalt not produced in metallic state on manufacturing scale. Obtained by simple ignition of the oxalate; by gentle ignition of the oxide in a current of hydrogen, or by its strong ignition in a charcoal-lined crucible. Metal, when containing carbon, fusible in forge fire; but, when free from carbon, fusible only at highest

heats. Cobalt a brilliant, reddish-tinted, grey or white metal, of sp. gr. 8·9, malleable, ductile, and more tenacious even than iron; more strongly magnetic than nickel, but less so than iron. Pulverulent metal, reduced at a low temperature by hydrogen, pyrophoric. Massive metal surface-tarnished, but otherwise unaffected, by exposure to air. Its slow oxidation at a red heat in air, and combustion at a red heat in oxygen gas. Its decomposition of steam at a red heat with evolution of hydrogen. Its gradual dissolution in aqueous hydrochloric and sulphuric acids with evolution of hydrogen. Its ready dissolution in nitric acid. Its assumption of passive state by immersion in strongest nitric acid.

Formation by cobalt of two well-defined series of compounds; a cobaltous or diad series typified by the chloride $CoCl_2$, and oxide CoO; and a cobaltic series typified by the oxide Co_2O_3, and the corresponding unstable chloride $CoCl_3$ or Co_2Cl_6. Existence also of a few intermediate, and yet superior compounds.

COBALTOUS OR COBALT COMPOUNDS.

Chloride, $CoCl_2$; produced in anhydrous state, as a crystalline sublimate, by heating cobalt in chlorine gas; and by decomposition of the oxichloride. Light blue spangles, unctuous to the touch, absorptive of water to form the pink hydrate, and prior to their hydration but very slowly soluble in water. Hydrated salt produced as above; and, most usually, by dissolving cobalt oxide in hot hydrochloric acid and evaporating the solution. Its occurrence as a hexahydrate $CoCl_2.6Aq$, in rose-pink, clino-rhombic prisms, isomorphous with those of corresponding nickel chloride.

Crystals decomposed by heat, with evolution of hydrochloric acid and formation of an oxichloride, resolved at higher temperatures into sublimed anhydrous chloride and residuary fixed oxide. Solubility of crystals in water to form a pink solution, turned blue by free addition of hydrochloric and sulphuric acids, probably through their action as dehydrating agents. Characters written on paper with dilute cobalt chloride solution almost invisible when cold, deep blue when heated, as a result of dehydration.

Oxide, CoO; made by strongly heating cobalt nitrate, hydrate, carbonate, or peroxide, and cooling the product in atmosphere of carbanhydride; or by igniting cobalt chloride in current of steam. A dark olive-green powder, reducible by hydrogen to metallic state, oxidisable by gentle ignition in air to state of $\frac{1}{4}$-oxide, and soluble in acids to form cobalt salts. The hydrate $CoO.H_2O$ or $Co(HO)_2$, made by precipitating cobalt chloride or nitrate with excess of potash or soda out of access of air. Precipitation at first of a blue basic salt, gradually changing into the rose-red hydrate. Its quick absorption of atmospheric oxygen. Combination of cobalt oxide with bases. Thénard's blue made by strongly igniting alumina with oxide or phosphate of cobalt. Rinmann's green made by strongly igniting mixed oxides of zinc and cobalt.

Sulphide, CoS. The anhydrous sulphide an unimportant compound, producible in various ways, and found native as the rare mineral syepoorite. The hydrated sulphide thrown down, by addition of alkali sulphide or sulphydrate to cobaltous solutions, as a dense black precipitate, not producible in presence of free acids, but when once formed difficultly soluble even in strong hydrochloric acid. Its gradual oxidation on exposure to air, with formation of cobaltous sulphate.

Arsenide, $CoAs$ or Co_2As_2; found native, in form of smaltine or tin-white cobalt, as the most abundant of cobalt ores. Its occurrence in metal-lustrous, white or pale-grey, masses and crystals of the regular system, of sp. gr. 6·6. Its habitual isomorphous admixture with more or less cloanthite $NiAs$ or Ni_2As_2.

Nitrate, $Co(NO_3)_2$; made by dissolving cobalt oxide or carbonate in nitric acid. A deliquescent, very soluble, rose-red salt, crystallising in rhombic tables with 6 molecules of water. Its decomposition by ignition to leave cobalt oxide. Its use in blowpipe analysis, especially for the recognition of aluminium, zinc, and magnesium compounds, rendered blue, green, and pale-pink respectively, when moistened with nitrate of cobalt solution and strongly ignited.

Carbonate, $CoCO_3$. The ordinary carbonate, thrown down from cobalt solutions by alkali carbonate as a pink precipitate, a hydrated basic salt of variable composition. Its solubility in acids to form different cobalt salts, decomposition on ignition to leave cobalt oxide, and reaction with chlorine to form the peroxide. Conversion of the freshly precipitated basic salt into the normal carbonate $3CoCO_3.2Aq$, by digesting it in solution of acid carbonate of sodium or ammonium.

Sulphate, $CoSO_4$; made by dissolving cobalt oxide or carbonate in sulphuric acid, and evaporating down. A soluble, efflorescent, rose-red salt, crystallising isomorphously with ordinary green vitriol in 7-hydrated clino-rhombic prisms; and also as a 6-hydrate, isomorphous with native sulphate of magnesium, &c. Salt easily rendered anhydrous; not further altered by moderate ignition. Its combination with sulphate of potassium to form the double salt $K_2Co(SO_4)_2.6Aq$.

Phosphate. The hydrated salt $Co_3(PO_4)_2.8Aq$, formed as a flocculent violet-red precipitate, by reaction of cobalt nitrate or chloride and sodium phosphate solutions. The corresponding arseniate $Co_3(AsO_4)_2.8Aq$, found native as cobalt bloom or erythrine, in radiated acicular crystals having a pearly lustre and variously tinted red colour.

Silicate. An indefinite double silicate of cobalt and potassium produced commercially as the well known pigment smalt. Cobalt ore roasted, but only partially, so as to effect an oxidation of nearly all the cobalt arsenide, but not of the less oxidisable nickel, copper, and iron arsenides. Roasted ore then fused with about an equal weight of potassium carbonate and double its weight of ground quartz. Result of the fusion a deep blue cobalt glass, overlying a metallic-looking mass of speiss afterward cast into ingots. The fused cobalt glass poured into cold water, and the thereby split up fragments crushed to a powder, afterwards finely ground between millstones revolving under water. The suspended smalt finally caused to subside in portions of different fineness and consequent colour, by letting the turbid liquor flow through a series of larger and larger depositing tanks, so as

to afford the successively more and more minute particles more and more time in which to subside.

Use of cobalt oxide for the production of sapphire-blue glass, &c. Its similar solution in fused borax or microcosmic salt, as in fused alkali silicate, to form glass or bead of a deep blue colour. Process made available as a blowpipe test for cobalt.

COBALTIC COMPOUNDS.

Chloride, $CoCl_3$ or Co_2Cl_6; an unstable compound, formed in solution by dissolving freshly precipitated hydrated cobaltic oxide in cold aqueous hydrochloric acid. A brown liquid, evolving chlorine spontaneously, and freely at a boiling heat, to leave pink solution of cobaltous chloride.

Oxide, Co_2O_3; a brownish-black powder produced by heating the hydrate to boiling point of mercury, and by cautious decomposition of cobaltous nitrate by heat. Its conversion into the $\frac{3}{4}$-oxide at a red heat. Its solution in heated hydrochloric acid with evolution of chlorine. Hydrated cobaltic oxide $Co_2O_3\ 2H_2O$, made by precipitating a cobaltous salt with alkali hypochlorite; or by passing chlorine gas through cobaltous oxide or carbonate suspended in water or preferably in caustic alkali:

$$2CoCl_2 + Ca\left\{\begin{matrix}Cl\\ClO\end{matrix}\right. + 2(CaO.H_2O) = 3CaCl_2 + Co_2O_3 + 2H_2O$$

Its occurrence after desiccation as a brown-black agglomerated mass or powder, dehydratable at a moderate heat, easily reducible into the $\frac{3}{4}$-oxide, soluble in not too dilute hydrochloric acid with evolution of chlorine, and in nitric and sulphuric acids with evolution of oxygen. Its oxidation of oxalic and sulphurous acids, &c. Its curious unlimited decomposition of hypochlorite solutions at a gentle heat, thereby rendering them available as sources of oxygen:

$$Ca\left\{\begin{matrix}Cl\\ClO\end{matrix}\right. = CaCl_2 + O$$

Combinations of cobaltic oxide with more basylous oxides. Preformed cobaltic oxide insoluble in caustic alkali. But produc-

tion apparently of a soluble potassium cobaltite, by moistening precipitated cobaltous oxide with aqueous potash under free exposure to air. A deep blue solution formed, becoming eventually colourless, gradually in the cold, rapidly at a boiling heat, with deposition of hydrated cobaltic oxide. Cobaltous cobaltite $CoO.Co_2O_3$ or Co_3O_4, made by ignition, under exposure to air, of both extreme oxides and of the several cobalt salts yielding them. Also, in hydrated state, by prolonged exposure to air of moist precipitated cobaltous oxide. The anhydrous compound a dense black powder, difficultly soluble in acids with evolution of oxygen or chlorine. The $\frac{3}{4}$-oxide reduced by strong ignition to state of protoxide, reconverted into $\frac{3}{4}$-oxide during cooling in contact with air. Alleged production of an intermediate oxide, Co_6O_7 or $3CoO.Co_3O_4$ or $4CoO.Co_2O_3$, probably a mixture of protoxide and $\frac{3}{4}$-oxide.

Cobalt-yellow. Production on adding nitrite of potassium to an acidulous solution of cobaltous nitrate, and by equivalent processes, of a bright orange-yellow crystalline powder, made up of microscopic four-sided needles with pyramidal summits. Composition and nature of the compound not established, usually expressed by cobaltic formula, $\left.\begin{matrix}Co_2O_3\\(K_2O)_3\end{matrix}\right\}(N_2O_3)_5.2H_2O$ (Stromeyer). Its use as a pigment for artistic purposes. Its insolubility in cold water, slow dissolution in boiling water with formation of a lemon-yellow salt, and decomposition by ebullition with strong nitric and hydrochloric acids to yield ordinary cobalt solutions. Precipitation of cobalt-yellow an excellent means of separating cobalt from other metals, especially nickel.

Cobalticyanides. Excess of cyanide of potassium, or preferably of hydrocyanic acid and caustic potash, added to cobaltous nitrate solution and liquid exposed to the air. Production, by oxidation, of potassium cobalticyanide $K_3\overset{'''}{Co}Cy_6$, analogous to the ferridcyanide $K_3\overset{'''}{Fe}Cy_6$:

$$2HCy + 6KCy + 2CoCy_2 + O = H_2O + 2K_3\overset{'''}{Co}Cy_6$$

Under same conditions, production with nickel nitrate of the soluble double cyanide $2KCy.NiCy_2$. Nickel of this compound precipitated by acids as nickel cyanide, by mercuric oxide as nickel oxide, and by excess of alkali hypochlorite, at boiling heat, as nickel peroxide. Cobalticyanide of potassium solution unaffected by all these reagents. But precipitation from it by mercurous nitrate of mercurous cobalticyanide, leaving residue of cobalt oxide upon ignition. Precipitation of nickel from the cyanide solution, by mercuric oxide or alkali hypochlorite, available for its separation from cobalt. Its precipitation by acids not directly available, through formation of an insoluble cobalticyanide of nickel.

Cobalticyanide of potassium obtainable, on evaporation of its solution, in yellowish flattened prisms, extremely soluble in water.

Cobaltamines. The precipitate, thrown down by ammonia from different cobaltous salts, soluble in excess of ammonia to form pale-brown rapidly oxidising solutions. Production from resulting oxidised red solutions, by their acidification and otherwise, of different series of complex ammonio-cobaltic salts, those of the same series being readily transformable into each other by ordinary saline decomposition. Chlorides of the best investigated series represented by the following formulæ, or by their doubles:

$H_2O.5NH_3.CoCl_3$	Roseo-cobaltic chloride
$5NH_3.CoCl_3$	Purpuro-cobaltic chloride
$5NH_3.Co(NO_2)''Cl_2$	Xantho-cobaltic chloride
$6NH_3.CoCl_3$	Luteo-cobaltic chloride
$H_2O.5NH_3.CoO''Cl_2$	Oxy-cobaltic chloride

Roseo-cobaltic chloride produced, as a heavy brick-red crystalline precipitate, by addition of hydrochloric acid to the red liquid obtained by exposing ammoniacal solution of cobaltous chloride to the air. Precipitate but sparingly soluble in hydrochloric acid; soluble in water to form a rose-red solution. The corresponding nitrate and sulphate procurable by similar processes.

Water of these salts possibly different from mere water of crystallisation (?).

Purpuro-cobaltic chloride, the most permanent of ammonio-cobaltic compounds. Produced by boiling with hydrochloric acid or sal-ammoniac the red liquid resulting from exposure to air of ammoniacal solution of cobaltous chloride; and also by boiling or keeping the solution of roseo-cobaltic chloride. Violet-red quadratic prisms, insoluble in strong hydrochloric acid hot or cold, almost insoluble in cold water, soluble in and crystallisable from boiling water acidulated with hydrochloric acid. All other purpuro-cobaltic compounds converted into the insoluble chloride by ebullition with hydrochloric acid. Difference between roseo- and purpuro- cobaltic chlorides probably similar to that between the two palladous ammonic, and the two platinous ammonic chlorides. (*q. v.*)

Xantho-cobaltic chloride produced by precipitating the corresponding sulphate with chloride of barium. Its conversion into above purpuro-chloride by ebullition with hydrochloric acid. The sulphate made by passing current of nitrous gas through red liquid resulting from exposure to air of ammoniacal solution of cobaltous sulphate. Its deposition from the liquid in form of yellow rhombic plates $5NH_3.Co(NO_2)SO_4$.

Luteo-cobaltic chloride made by adding powdered sal-ammoniac to ammoniacal solution of cobaltous chloride, oxidising liquid by exposure to air, or preferably by boiling it with peroxide of lead, and acidifying produced liquid with hydrochloric acid. Gradual deposition of the salt in yellow needles.

Oxycobaltic chloride not isolable by reason of its great solubility. The corresponding nitrate $H_2O.5NH_3.CoO(NO_3)_2$, produced spontaneously, in olive-brown prisms, by exposure of ammoniacal solution of cobaltous nitrate to the air.

PER-COBALTIC COMPOUNDS.

Correspondence of the above nitrate, $H_2O.5NH_3.CoO(NO_3)_2$, and of other oxy-cobaltic salts, to an unknown cobalt dioxide

CoO_2, instead of to the sesquioxide Co_2O_3, or its equivalent chloride Co_2Cl_6 or $CoCl_3$.

Again, a compound, expressible by formula $K_2Co_9O_{16}.3Aq$, left in form of insoluble lustrous black crystals by heating cobalt oxide or carbonate with fused caustic potash. Presumed existence in these crystals of cobalt dioxide, thus $\left.\begin{matrix}K_2O\\3CoO\end{matrix}\right\}6CoO_2$.

Cobaltine or cobalt-glance CoAsS (isomorphous with iron pyrites FeS_2, in the regular system), an analogue of cobalt dioxide. Its occurrence in compact masses and well-defined modified cubical crystals, of sp. gr. 6·3, and metal-lustrous reddish-tinted white or grey colour.

Cobalt compounds, in solid state, recognised by their blue coloration of the borax-bead. Cobaltous solutions recognised by their well-marked pink colour, becoming blue on evaporating the solutions with excess of acid. Also, by their affording with sulphide of ammonium a black precipitate of cobaltous sulphide difficultly soluble in hydrochloric acid; with ammonia and salammoniac a pink precipitate dissolving in excess to form a red solution not precipitable by potash; with cyanide of potassium a pinkish precipitate dissolving in excess to form a solution unaffected, after its exposure to air, by addition of hydrochloric acid; with alkali hypochlorites a black precipitate of cobaltic oxide, producible in acidulous solutions; and with nitrite of potassium a characteristic precipitate of cobalt-yellow.

(92.) Nickel.

For distribution of nickel, and isolation of its oxide, carbonate, oxalate, &c., *vide* Cobalt. Its production in metallic state. On manufacturing scale, small lumps of dried up nickel oxide, together with powdered charcoal, introduced into vertical fire-clay cylinders set in a furnace. Consequent reduction of nickel oxide by the produced carbonous oxide gas. Reduced metal, in form of original small lumps of oxide, withdrawn from time to time through temporarily closed holes in conical bottoms of the

cylinders. Nickel also obtainable by way of electrolysis; by ignition of nickel oxalate; by gentle ignition of nickel oxide in a current of hydrogen; or by its strong ignition in a charcoal-lined crucible. Fusibility of nickel, as of iron, increased by its combination with small proportion of carbon. Pure metal very refractory, but fusible in strongest heat of a wind furnace.

Fused nickel a silver-white, hard, malleable, ductile, and extremely tenacious metal, of sp. gr. 8·6; paramagnetic at ordinary temperatures, but ceasing to be so at 250° and upwards. Pulverulent metal, as reduced from nickel oxide at a low temperature by hydrogen or carbonous oxide, readily oxidisable and even pyrophoric. Compact metal tarnishable in moist air, but not further oxidisable save at a red heat. Its combustion at a red heat in oxygen gas. Its decomposition of steam at a strong red heat, with evolution of hydrogen. Its somewhat slow dissolution in aqueous hydrochloric and sulphuric acids, with evolution of hydrogen. Its ready dissolution in nitric and nitro-muriatic acids. Metal rendered passive by immersion in strongest nitric acid.

Chief use of nickel for alloying with copper and zinc, so as to produce a kind of white brass, known as German silver, harder than true silver and susceptible of a high polish. Extensive employment of the alloy as a substitute for silver, whether or not coated electrolytically with silver. Proportions of constituent metals very various, usually within the limits of 50 to 60 per cent. copper, 20 to 30 per cent. zinc, and 15 to 20 per cent. nickel. A Chinese nickel-silver, containing only 40 per cent. of copper, known as packfong. German silver made by adding zinc to fused mixture of copper and nickel. Alloy crystalline after fusion, but rendered malleable, and capable of being worked like brass, by being heated to dull redness and allowed to cool.

Formation by nickel of but one series of salts, typified by the diad chloride $NiCl_2$, and oxide NiO. Existence, however, of a few compounds appertaining to other series, as the sulphides Ni_2S and NiS_2, the oxide Ni_2O_3, &c.

Chloride, $NiCl_2$; obtainable by heating the hydrated salt; and, as a sublimate of golden yellow scales, by igniting nickel filings in a current of chlorine. Dissolution of the sublimate in water, only after prolonged ebullition, to form the ordinary green solution. The hydrated salt best made by dissolving nickel oxide, hydrate, or carbonate in hydrochloric acid, or metallic nickel in nitro-muriatic acid. Deposition of the hydrate $NiCl_2.9Aq$, in fine green crystals, upon evaporation of the so produced solution. Existence also of a hexahydrate.

Oxide, NiO; made by strongly igniting the nitrate, carbonate, or hydrate. A dark greenish-grey powder, not absorptive of oxygen at any temperature. Rare occurrence of the native oxide, crystallised in minute regular octahedrons. The hydrate $NiO.H_2O$ or $Ni(HO)_2$, thrown down from solutions of nickel salts by fixed caustic alkali, as a flocculent apple-green precipitate. Also deposited, as a green crystalline powder, by evaporation of solution of nickel carbonate in ammonia. Dehydration of the compound by heat; and its ready solution in acids to form nickel salts. Its solubility also in ammonia to form a blue-purple liquid, resembling a dilute ammoniacal cupric solution. Hydrated nickel oxide, retaining some fixed alkali, thrown down by addition of potash to above ammoniacal solution.

Peroxide, Ni_2O_3; produced, in anhydrous state, by careful heating of nickel nitrate. Its decomposition by ignition into nickel oxide and oxygen. Nickel peroxide, or its hydrate, also thrown down as a dense black precipitate, by addition of alkali hypochlorite to boiling solution of double potassio-nickel cyanide. The hydrate $Ni_2O_3.3H_2O$, producible as a brown-black precipitate, by decomposing ordinary nickel solutions with mixed alkali hydrate and hypochlorite. Dissolution of the peroxide, hydrated or anhydrous, in hydrochloric acid with evolution of chlorine, and in sulphuric and nitric acids with evolution of oxygen, to furnish ordinary nickel salts.

Sulphide, NiS; found native, as haarkies or capillary pyrites, in brass-yellow fibres and rhombohedrons. Made, in hydrated

state, by action of alkali sulphide or sulphydrate on dissolved nickel salts. A flocculent black precipitate, not formed in presence of free acid, even of the acetic; but, when once thrown down, insoluble, or almost so, even in boiling hydrochloric acid. Its oxidation on exposure to air to yield nickel sulphate.

A subsulphide of nickel Ni_2S, analogous in composition to cuprous sulphide, produced as a yellow lustrous mass by igniting nickel sulphate in a current of hydrogen. A persulphide of nickel NiS_2, analogous in composition to iron pyrites, left in the form of a steel-grey powder by igniting mixture of nickel carbonate, potassium carbonate, and sulphur, and washing away soluble salts.

Arsenide, Ni_3As_2. Correspondence of purest specimens of speiss to this formula. Occasional production of speiss in well defined di-metric prisms. Its usual occurrence as a brownish-grey, metallic-looking, fusible mass. Kupfer-nickel Ni_2As_2 or NiAs, the principal ore of the metal. A lustrous coppery-red mineral, of sp. gr. 7·3, found massive, and more rarely crystallised in hexagonal prisms. Cloanthite, or white nickel, $NiAs_2$, a lustrous tin-white mineral, of sp. gr. 6·4, found massive, and crystallised in the regular system. Nickel glance NiAsS, a lustrous white or grey mineral, also crystallising in regular forms, chiefly cubical. Partial and even complete replacement of arsenic by antimony in some specimens. Hence variation of sp. gr. from 5·6 to 6·9. Breithauptite Ni_2Sb_2 or NiSb, the antimonide corresponding to kupfer-nickel, met with massive, and crystallised in hexagonal plates.

Nitrate, $Ni(NO_3)_2$; made by dissolving the metal or oxide in nitric acid. Its crystallisation in emerald-green needles, freely soluble in water.

Carbonate, $NiCO_3$; produced, as a greenish-white crystalline powder, on pouring dissolved nickel salt into large excess of sodium acid-carbonate solution. The amorphous compound, thrown down from nickel solutions by alkali carbonates, a basic or hydrate- carbonate of variable composition, approximating to $Ni_2(HO)_2CO_3$. Its deposition as an apple-green flocculent preci-

pitate, drying up into a loose earthy mass, soluble in dilute acids with effervescence to form nickel salts.

Sulphate, $NiSO_4$; made by dissolution of metallic nickel in nitro-sulphuric acid. Its crystallisation, at and below 15°, as a heptahydrate $NiSO_4.7Aq$, in green orthorhombic prisms, isomorphous with those of Epsom salt. Small quadratic octahedrons of the hexahydrate $NiSO_4.6Aq$, deposited between 15° and 20°, and also produced by spontaneous breaking up of the heptahydrate. The hexahydrate dimorphous, and producible in clino-rhombic prisms isomorphous with hexahydrated magnesian sulphate. Crystallised nickel sulphate, rendered yellow, amorphous, monohydrated, and finally anhydrous at a moderate heat. Its free solubility in water. Its combination with potassium sulphate, ammonium sulphate, &c. to form double salts, as $K_2Ni(SO_4)_2.6Aq$, isomorphous with magnesian double sulphates. The potassium double sulphate a readily crystallisable salt, producible by dissolving speiss in dilute sulphuric acid, with aid of a little nitric acid from time to time, adding sufficiency of carbonate of potassium, setting aside so as to allow much arsenious oxide to deposit, and evaporating down.

Nickel compounds, in solid state, recognisable before the blowpipe by giving to the borax bead a peculiar reddish-tinted sherry colour, becoming amethystine on addition of a fragment of nitre. Nickel solutions characterised by their marked green colour. Also, by their giving with sulphide of ammonium a black precipitate, slightly soluble in excess of the reagent, scarcely soluble in hydrochloric acid; and with ammonia, a pale green precipitate, dissolving in excess to form a violet-blue solution, yielding a green precipitate on addition of potash. Greenish precipitates also produced in nickel solutions by alkali hydrate, carbonate, oxalate, ferrocyanide, &c.

(93.) COPPER.

Copper an element of considerable abundance and very wide distribution. Native reguline copper met with to a small extent in many localities, and to large extent in neighbourhood of Lake Superior, so as to constitute a valuable commercial source of the metal. Malachite $Cu_2(HO)_2CO_3$, the chief copper ore of South Australia; also found largely in Siberia. The most important English ores, copper pyrites $Cu_2Fe_2S_4$, and phillipsite or purple ore $Cu_6Fe_2S_6$, obtained chiefly from Cornwall and Anglesea. Existence of many other copper ores habitually or occasionally smelted, and found for the most part in association with the preceding; namely, cuprous oxide Cu_2O, or red ore; cupric oxide CuO, or black ore; copper glance Cu_2S, or vitreous ore; covellite CuS, or indigo ore; tetrahedrite $Cu_4Sb_2O_5$, or grey copper; azurite $Cu_3(HO)_2(CO_3)_2$, or blue ore; dioptase $CuSiO_3.Aq$, and chrysocolla $CuSiO_3.2Aq$, or emerald ore, &c. Various other copper compounds met with as more or less definite minerals.

Copper, to a greater or less extent, almost constantly associated with iron, nickel, and cobalt in their several arseniuretted and sulphuretted ores; and met with as a minor constituent of many and various other minerals. Traces of copper very generally recognisable in earth and water, including sea-water; and in animal and vegetable tissues.

Copper smelting a very complex operation, habitually modified in its conduct according to nature of the ores under treatment. Process substantially as follows. Mixture of sulphurous ores, selected so as to contain about 15 per cent. of copper, roasted at a low temperature in 'calcining furnace.' Cuprous sulphide thereby left unaltered, but iron sulphide converted largely into iron oxide and sulphurous anhydride. Roasted ore then fused in 'ore furnace' with silicious non-sulphurous ore and slag from later stage of a previous smelting (fine metal slag). Production in this way of a copper-free slag of iron silicate, and a heavy fused mixture of cuprous sulphide with variable proportion of iron sulphide known

as matt, regulus, or 'coarse metal,' and containing from 30 to 36 per cent. of copper.

Subsequent calcination of granulated coarse metal, with further conversion of the iron sulphide into iron oxide and sulphurous anhydride. Calcined coarse metal then heated in 'melting furnace' with rich non-sulphurous copper ore, and rich copper slags from roasting and refinery furnaces. By this means iron completely separated as a silicated slag (retaining, however, a minute proportion of copper) from the regulus or matt of 'fine metal,' consisting mainly of cuprous sulphide, and containing from 70 to 80 per cent. of metallic copper. Essence of process up to this point, conversion of the entire copper, whether or not originally sulphurous, into form of cuprous sulphide; oxidation of the iron, partly by air, partly by the copper oxide of non-sulphurous ores and slags, and its entire removal in form of silicate; correlative desulphuration of the iron sulphide, partly by oxidation and removal of its sulphur, partly by the union of its sulphur with the copper of non-sulphurous copper ores and slags.

Fine metal cast into pigs, afterwards heated for some hours on floor of 'roasting furnace' at temperature just insufficient to melt them. Portion of cuprous sulphide thereby converted into cupric oxide and sulphurous anhydride. Eventual fusion of the charge, with reaction of remaining cuprous sulphide and produced cupric oxide to yield metallic copper:

$$Cu_2S \quad + \quad 2CuO \quad = \quad 4Cu \quad + \quad SO_2.$$

Temperature then raised, and reduced metal cast into ingots of 'blistered copper,' so called from its vesicular structure resulting from continued evolution of interstitial sulphurous gas.

Blistered copper then kept melted for many hours in 'refining furnace,' to effect the complete oxidation and removal of foreign and more oxidisable metals. Consequent production of a rich copper slag, and dissolution of some cuprous oxide in the melted metal. Slag skimmed off, and metal subjected to process of 'poling' or stirring up with trunk of a young tree. In this way, the copper completely deoxygenated by action of evolved com-

bustible gases. Result of poling process tested from time to time, by ladling out a portion of the metal, cooling it by immersion in water, hammering the button, cutting it half-through with a chisel, and then bending it across so as to exhibit its structure. Properly poled copper tough, finely fibrous, and presenting a uniform silky lustre on its torn surface. Under-poled copper brittle, granular, and irregularly punctated from presence of cuprous oxide. Over-poled copper brittle, coarsely fibrous, and wanting in silky lustre. Nature of defect by over-poling unexplained; remedied by heating the melted metal in current of air.

Presence of some copper in much foreign pyrites used for vitriol making, so as to leave from 2 to 4 per cent. and upwards of copper in the burnt residue. This residue mixed with common salt and heated to dull redness for some hours in ovens or furnaces. Consequent conversion of the copper into form of chloride or oxichloride left in the oven, and evolution of chlorides of hydrogen, sulphur, arsenic, and iron, with trace of chloride of copper, collected in flues and condensing towers. Contents of ovens extracted with water acidified with acid liquor of condensing towers, and copper of the resulting impure chloride solution precipitated in metallic state by scrap-iron. Insoluble residue from the ovens, consisting of sulphur- and arsenic-free ferric oxide, used for lining forge furnaces, smelting in blast furnaces, &c.

The copper frequently present in drainage waters pumped up from copper mines, recovered by allowing the water to flow over scrap iron.

Pure copper readily obtainable by electrolysing pure cupric sulphate solution.

Copper the only metal of a red colour. Crystallisation of native copper, and of metal slowly reduced from solution, in forms of the regular system. Hardness of copper inferior to that of soft iron. Its ductility and malleability very great; whence its habitual production in state of very fine wire and thin leaves. Its hardness much increased by drawing or hammering, but reduced again by subsequent heating to redness. Its tenacity, though little more than half that of iron, very considerable, superior

to that of any other common metal. Conductivity of copper very high; inferior to that of silver, only in proportion of 93 to 100; but much impaired by presence of even minute impurities. Sp. gr. of copper 8·93 to 8·95. Habit of the metal, melted under charcoal and cast in air, to acquire a vesicular structure from formation of interstitial carbonous oxide, lowering its sp. gr. even to 6 or 7. Fusion of copper at temperature intermediate between melting points of silver and gold. Its extreme brittleness at a little below its melting point. Its volatilisation at an intense heat.

Unoxidisability of copper by exposure to dry air; save at, or near to, a red heat. Its acquisition of a layer of scaly oxide by ignition in air; and its combustion, even, when in finely divided state. Its acquisition of a green coating of basic carbonate (natural verdegris) by exposure to moist air. Its but slight decomposition of vapour of water, even at a bright red heat. Its ready combination at a red heat with sulphur and phosphorus, and decomposition of sulphuretted and phosphoretted hydrogen. Its rapid attackability by chlorine, bromine, and iodine; the action of chlorine on finely divided copper being frequently attended with combustion. Copper unacted upon by dilute sulphuric or hydrochloric acid. Its slow dissolution, when in finely divided state, in boiling concentrated hydrochloric acid, with formation of cuprous chloride and evolution of hydrogen. Its reaction with heated strong sulphuric acid to form sulphurous anhydride and a mixed sulphate and oxisulphide of copper. Its indifference to the strongest nitric acid; but dissolution in the slightly diluted acid, as cupric nitrate, with evolution of nitric oxide gas. Copper readily attackable by even very dilute and weak acids, under free exposure to air; also, under the same exposure, by various saline and alkaline solutions. Its considerable dissolution in aqueous ammonia, under exposure to air, with formation of a deep blue liquid.

Alloys of copper with aluminium, tin, and nickel already referred to. Brass, an important alloy of copper with zinc, ordinarily made by adding half its weight of zinc to melted copper;

but also producible, without fusion, by exposing copper to zinc vapour, igniting copper in contact with zinc oxide and charcoal, &c. Composition of ordinary brass in approximate accordance with the formula Cu_2Zn, but liable to considerable range of variation. Its fusion at or below the melting point of copper, with greater or less alteration of composition through some volatilisation of zinc. Its hardness usually superior to that of copper (?), but inferior to that of gun-metal. Its sp. gr. 8·29, above the mean specific gravity of its constituents. Brass brittle at a red heat, malleable and ductile at ordinary temperatures, some varieties more so than copper itself. Ready working of brass by stamping, casting, turning in a lathe, &c. Effect of hammering or stamping to render the metal hard and brittle; whence necessity for its frequent annealing during the process.

Brass more resistant of atmospheric influences than copper. Its indifference to dilute sulphuric and hydrochloric acids; but, notwithstanding its large proportion of copper, entire solubility in strong hydrochloric acid with evolution of hydrogen and formation of cuprous and zinc chlorides. Its non-precipitation of copper from cupric solutions.

A variety of brass known as 'yellow-metal,' containing 40 per cent. zinc and 60 per cent. copper, largely used for coating ships' bottoms. Aich-metal, a very hard yellow metal, containing instead of 40 per cent. zinc, 38·2 per cent. zinc and 1·8 per cent. iron. Sterro-metal, a similar alloy, containing 0·8 per cent. tin, 1·8 per cent. iron, 42·4 per cent. zinc, and 55 per cent. copper. Brass solder, an alloy of brass with half its weight of zinc. Frequent addition of a little tin to the brass used for door-plates, &c., and of a little lead to brass having to be turned in a lathe.

Formation by copper of two well-defined series of compounds. Existence of a monad or quasi-monad or cuprous series of compounds, having a marked resemblance to compounds of silver, and typified by cuprous sulphide Cu_2S, the oxide Cu_2O, and the chloride $CuCl$ or Cu_2Cl_2; and of a diad or cupric series of compounds having a marked analogy to compounds of nickel, and typified by cupric oxide CuO, and the chloride $CuCl_2$.

CUPROUS COMPOUNDS.

Hydride, CuH or Cu_2H_2; made by heating solution of mixed cupric sulphate and hypophosphorous acid to below 70°. A yellow-brown precipitate, in moist state tolerably stable, in dry state decomposible at 60° with some violence, and gradually at lower temperatures. Its curious solubility in hydrochloric acid with evolution of hydrogen:

$$CuH \quad + \quad HCl \quad = \quad CuCl \quad + \quad H_2$$

Chloride, CuCl or Cu_2Cl_2; producible by various dechlorinations of cupric chloride, and in other ways. Best made by dissolving mixture of cupric oxide and copper turnings in hydrochloric acid, and pouring resulting liquid into large excess of water. A dense, crystalline, white powder, becoming blue by exposure to air, melting below a red heat, and solidifying into a yellowish translucent mass. Its insolubility in water. Its solubility in hydrochloric acid, free solubility in the heated acid, and deposition on cooling of the solution in well-defined regular octahedrons. Its combination with chlorides of potassium, sodium, ammonium, &c., to form colourless, soluble, crystallisable, double salts, such as CuCl.2KCl. Its solubility also in excess of ammonia, especially in presence of chloride of ammonium, as a cuprosammonium compound. Rapid coloration, at first brown and then green or blue, of cuprous solutions under exposure to air. Absorption of carbonous oxide by cuprous chloride and its hydrochloric acid solution, with formation of a crystalline compound, $2CuCl.CO.H_2O$. Dissolution of finely divided metallic copper in boiling sal-ammoniac solution, with evolution of ammonia. Gradual deposition of the salt $NH_3.CuCl$ or $2NH_3.Cu_2Cl_2$, in white, rhombohedral crystals.

Iodide, CuI or Cu_2I_2; the only known iodide of copper. Producible, together with free iodine, by addition of potassium iodide to cupric sulphate solution; best made by addition of the potassium salt to mixed cupric and ferrous sulphate solution:

$$2CuSO_4 \quad + \quad 4KI \quad = \quad 2K_2SO_4 \quad + \quad 2CuI \quad + \quad I_2$$

$$2CuSO_4 \quad + \quad 2KI \quad + \quad 2FeSO_4 \quad = \quad K_2SO_4 \quad + \quad 2CuI \quad + \quad Fe_2(SO_4)_3$$

A greyish-white precipitate, fusible at a red heat; readily yielding its iodine to basylous metals with separation of copper, and its copper to oxidising agents with separation of iodine.

Oxide, Cu_2O; found native as red copper or copper bloom, &c., crystallised in regular octahedrons or cubes, and in capillary filaments, of sp. gr. 6·0. Made in various ways, as by igniting mixture of cupric oxide with reduced copper, or of cuprous chloride with sodium carbonate and washing away soluble salts. Also, at first as an unstable orange hydrate, by boiling a solution of mixed cupric sulphate, grape sugar, and caustic alkali. Artificial cuprous oxide a chocolate-red powder, fusible at a red heat, easily oxidisable to the state of cupric oxide when heated in a current of air, and reducible to the state of metallic copper when heated in a current of hydrogen. Existence of a few cuprous oxisalts; but decomposition of cuprous oxide by most oxacids with formation of cupric salt and metallic copper:

$$Cu_2O = CuO + Cu$$

Use of cuprous oxide in production of a ruby-red glass, liable to become green by oxidation.

Sulphide, Cu_2S; found native as copper-glance or redruthite, both massive and crystallised in flat orthorhombic prisms. Made by direct combination of copper with heated sulphur, and in other ways. Crystallisation of artificial compound in regular octahedrons (Mitscherlich). Production of cuprous sulphide on large scale, in copper smelting, as 'fine-metal.' Fused cuprous sulphide a grey, lustrous, sectile mass, of sp. gr. 5·9. Its oxidation, when heated in a current of air, to produce cupric oxide; or, at a low temperature, cupric sulphate. Its reactions, when heated with cupric oxide, to furnish cuprous oxide or metallic copper:

$$Cu_2S + 6CuO = 4Cu_2O + SO_2$$
$$Cu_2S + 2CuO = 4Cu + SO_2$$

Double sulphides. Combination of cuprous sulphide as a sulpho-base with more chlorous sulphides or sulphanhydrides to

form definite cuprous sulpho-salts, many of them found native as the following:

$Cu_2S.Bi_2S_3$	or	$CuBiS_2$	Tannenite
$3Cu_2S.Bi_2S_3$	„	Cu_3BiS_3	Wittichenite
$Cu_2S.Sb_2S_3$	„	$CuSbS_2$	Wolfsbergite
$2Cu_2S.Sb_2S_3$	„	$Cu_4Sb_2S_5$	Fahl-ore?
$2PbS.Cu_2S.Sb_2S_3$	„	$PbCuSbS_3$	Bournonite
$3Cu_2S.As_2S_3$	„	Cu_3AsS_3	Tennantite

Frequent isomorphous replacement, in different cuprous sulpho-salts, of some cuprosum by various other metals. Different varieties, for example, of the mineral known as tetrahedrite, fahl-ore, grey-copper, &c., complex sulphantimonites and sulpharsenites of mutually replaceable cuprosum, silver, lead, zinc, and iron, crystallised together in modified tetrahedral forms. Isomorphism of silver-copper glance CuAgS, with native copper glance Cu_2S, in the right prismatic system; and of silver glance Ag_2S, with artificial cuprous sulphide Cu_2S in the regular system. Polybasite a complex superbasic sulphantimonite of mutually replaceable silver and cuprosum:

$$9(Ag,Cu)_2S.Sb_2S_3 \quad \text{or} \quad (Ag,Cu)_9SbS_6 \quad \text{or} \quad (Ag,Cu)_3SbS_3.3(Ag,Cu)_2S$$

Ordinary copper pyrites $CuFeS_2$ or $Cu_2Fe_2S_4$, the principal copper ore of the Cornish mines, usually represented as a cuprous sulpho-ferrite $Cu_2S.Fe_2S_3$, analogous to cuprous sulphantimonite or wolfsbergite $Cu_2S.Sb_2S_3$. Found in massive state; and crystallised in tetrahedrons &c. belonging to the square prismatic system. Its sp. gr. 4·1. Its colour brass-yellow, like that of iron pyrites. Its hardness much inferior to that of iron pyrites, shown by its capability of being cut with a knife. Its weathering, under exposure to air, to furnish mixed cupric and ferrous sulphates. Its attackability by nitric acid with separation of sulphur. Proportion of copper in pure iron pyrites 34·6 per cent. Other iron-copper sulphides, containing from 55 to 70

per cent. of copper, known as purple copper, phillipsite, &c. Inclusion under these names of copper ores referrible to the formula $Cu_6Fe_2S_6$ or $3Cu_2S.Fe_2S_3$; of still richer ores referrible to the formula $Cu_{18}Fe_2S_{12}$ or $9Cu_2S.Fe_2S_3$; and of various intermediate ores, most often containing about 63 per cent. of copper; all the differently constituted compounds closely resembling each other and crystallising in forms of the regular system.

Doubtfully warrantable reference to the cuprous series of several ill-defined copper phosphides. Formation of a lustrous black phosphide, by boiling phosphorus in cupric sulphate solution. Its indifference to hydrochloric acid; solubility in aqueous cyanide of potassium, with evolution of spontaneously inflammable phosphoretted hydrogen. Production of an inflammable, electrolytically conductive phosphide, by passing vaporised phosphorus over finely divided metallic copper at a gentle heat. Its use in the construction of Abel's fuses, fired by the magneto-electric current.

CUPRIC COMPOUNDS.

Fluoride, CuF_2; made by dissolving cupric oxide or carbonate in hydrofluoric acid. Light blue crystals, decomposed by boiling water to leave the fluor-hydrate $CuF(HO)$, as an apple-green insoluble powder.

Chloride, $CuCl_2$; made, in anhydrous state, by action of dry chlorine on metallic copper; and by desiccation of the hydrate at 200°. A yellow-brown solid, fusible with care, decomposible at a red heat into cuprous chloride and chlorine gas. Its deliquescence in air, to form the green hydrated salt. Usual formation of this salt $CuCl_2.2Aq$, by dissolving cupric oxide, hydrate, or carbonate in hydrochloric acid and evaporating. Its deposition in grass-green needles, very deliquescent and soluble in water to form a bright green liquid, rendered bluish by considerable dilution. Cupric chloride also freely soluble in alcohol, to form a solution burning with a fine green flame. Combination of cupric chloride with alkali chlorides to form crystallisable double salts as $NH_4Cl.CuCl_2.2Aq$, $2NH_4Cl.CuCl_2.2Aq$, $2KCl.CuCl_2.2Aq$, &c.

Absorption of ammonia by anhydrous cupric chloride to form the blue compound $6NH_3.CuCl_2$, giving off some of its ammonia on exposure to air. A hydrated ammonia compound $4NH_3.CuCl_2.H_2O$, deposited in dark blue octahedrons, by passing ammonia gas through boiling aqueous cupric chloride until disappearance of the precipitate at first produced, and setting aside. Both the above compounds converted by a heat of 140°–150° into an apple-green pulverulent di-ammonia residue $2NH_3.CuCl_2$. The double salt $NH_4Cl.2NH_3.CuCl_2$, deposited in blue cubical crystals from the solution of pulverulent copper in sal-ammoniac, exposed to the air.

Oxide, CuO; found native as melaconite, sometimes crystallised in octahedrons, generally in massive state. Its formation artificially by heating metallic copper to dull redness in a current of air; by gently heating the hydrate or carbonate, igniting the nitrate, or very strongly igniting the sulphate; and by precipitating dissolved cupric salts with alkali at a boiling heat. Cupric oxide usually produced in form of a black hygroscopic powder, or of hard scaly or granular masses, of sp. gr. 6·3. Its fusion without change at a strong red heat. Its easy reduction by combustible substances at a very moderate heat, whence its general employment, in the combustion-analysis of organic bodies. The reduction of gently warmed pulverulent cupric oxide in an atmosphere of hydrogen attended with ignition. Its reduction by ignition with metallic copper, to form cuprous oxide. Its solubility in the mineral acids to form cupric salts. The hydrated oxide $CuO.H_2O$, sometimes produced by digesting the carbonate in cold caustic potash; usually made by precipitating the cold dilute solution of a cupric salt with excess of alkali, washing with cold water, and drying spontaneously in the air. A flocculent pale blue precipitate, drying up into greenish-blue friable masses, frequently brown at the edges from partial dehydration. Complete dehydration of the precipitate, as first thrown down, by its ebullition with water; of the dried precipitate by a heat of 120°. Ready solubility of cupric hydrate in aqueous ammonia, to form a deep purple-blue solution rendered colourless by digestion with metallic copper. A hydrated oxichloride of copper $Cu_4O_3Cl_2.4H_2O$,

found native in green orthorhombic prisms as atacamite; and produced artificially, in pulverulent state, by exposing copper clippings moistened with hydrochloric acid to the air, as a valuable bright green pigment (Brunswick green), unalterable by the action of sunlight.

Sulphide, CuS; found native as covellite or indigo copper ore, in hexagonal plates, more commonly in spheroidal masses, of bluish-black colour and sp. gr. 4·6. Its conversion by roasting, at a low temperature into cupric sulphate, at a high temperature into cupric oxide and sulphurous anhydride. Frequent presence of some cupric sulphide as a substitute for cuprous sulphide, in the grey coppers or fahl-ores.* Cupric sulphide produced in hydrated state, by precipitating cupric solutions with sulphuretted hydrogen or alkali sulphide, as a brown-black precipitate; insoluble in dilute, soluble in stronger mineral acids; slightly soluble in sulphide of ammonium; oxidisable by exposure to air into cupric sulphate.

Nitrate, $Cu(NO_3)_2$; usually made by dissolving metallic copper in nitric acid and evaporating. Crystallisation at 20°–25°, of the terhydrate $Cu(NO_3)_2.3Aq$; at below 20°, of the hexahydrate $Cu(NO_3)_2.6Aq$. Bright blue prismatic crystals, fusing at 114°, deliquescent, and very soluble both in water and alcohol. Rapid oxidation of tin-foil by cupric nitrate, with phenomenon of combustion. Production of the nitrate-hydrate $Cu_2NO_3(HO)_3$, as a green insoluble powder, by heating the normal nitrate to 200°–300°; by boiling its solution with precipitated cupric oxide; and, somewhat curiously, by drenching cupric oxide with the strongest nitric acid. Its solubility in dilute nitric acid to reform the normal salt; and decomposition by ignition to leave cupric oxide.

Carbonates. The normal carbonate unknown. Existence in nature of three basic salts $Cu_3(CO_3)_2(HO)_2$, azurite or chessylite; $Cu_2(CO_3)(HO)_2$, malachite; and $Cu_2(CO_3)O$ (?), mysorine. Occurrence of azurite in small dark blue prismatic crystals. Malachite a very abundant pale green mineral, occasionally crystalline, usually compact and botryoidal. A carbonate-hydrate

having the composition of malachite, produced artificially by decomposing sulphate of copper and carbonate of sodium solutions at a boiling heat. The natural and artificial compounds alike decarbonated and dehydrated by prolonged ebullition with water.

Sulphate, $CuSO_4$; known, in hydrated state, as blue copperas or blue vitriol. A salt of large commercial importance, made in process of silver refining by immersing plates of copper in sulphate of silver solution; also by boiling metallic copper with but slightly diluted sulphuric acid in an iron pot; and by roasting artificial cuprous sulphide (got by heating old copper with sulphur) at a low temperature, and dissolving the product of mixed sulphate and oxide in diluted sulphuric acid:

$$Cu_2S + O_5 = CuSO_4 + CuO$$

Cupric sulphate also obtainable by roasting copper smelters' 'coarse metal,' extracting with water and crystallising. Copper of ferruginous mother-liquor usually precipitated by scrap iron, and then dissolved in sulphuric acid; or the mother-liquor evaporated down, and crop of mixed iron and copper sulphate crystals dried and gently ignited, so as to decompose the iron sulphate and leave the copper sulphate, to be afterwards dissolved by water and crystallised.

The hydrated sulphate $CuSO_4.5Aq$, crystallisable in bright blue anorthic prisms and tables. Crystallisation of cupric sulphate with excess of ferrous sulphate in heptahydrated, and of ferrous sulphate with excess of cupric sulphate in pentahydrated crystals, having the characteristic forms of the respective prevailing salts. Ordinary blue vitriol converted into the pulverulent monohydrate at 100°, not rendered anhydrous below 200°. The anhydrous compound an almost white powder, absorptive of water with great development of heat, and in frequent use as a desiccating agent. Its unalterability by a dull red, but decomposition by a full red heat to leave residue of cupric oxide. The hydrated salt soluble in $3\frac{1}{2}$ times its weight of cold, and in yet smaller quan-

tity of hot water to form a bright blue solution. Its insolubility in alcohol.

Combination of cupric sulphate with sulphates of potassium and ammonium to form double 6-hydrated salts as $K_2Cu(SO_4)_2.6Aq$, isomorphous with the magnesian double sulphates, &c. Existence of different basic cupric sulphates. The salt $Cu_3SO_4(HO)_4$, formed, as a green precipitate, by boiling hydrated cupric oxide in excess of cupric sulphate solution. Its occurrence, with added atom of water, as langite. The salt $Cu_4SO_4(HO)_6$, found native as brochantite, sometimes also with an added atom of water.

Absorption of ammonia by anhydrous cupric sulphate to form the compound $6NH_3.CuSO_4$, giving off some of its ammonia on exposure to air. The compound $4NH_3.CuSO_4.H_2O$, formed in dark blue crystals by adding excess of ammonia to cupric sulphate solution and evaporating. Action of a gentle heat on both compounds to leave the di-ammonia compound $2NH_3.CuSO_4$ (*vide* ammonia cupric chlorides).

Phosphates. Production of a pale blue precipitate by decomposing cupric sulphate with sodium phosphate solution. Several basic phosphates found native, including liebethenite $Cu_2(PO_4)HO$. The well-known pigment, Scheele's green $CuHAsO_3$, a hydro-cupric arsenite, formed by precipitating cupric sulphate with arsenite of potassium solution. Schweinfurt green $Cu_2\left\{\begin{matrix}(AsO_2)_2\\ H_3C_2O_2\end{matrix}\right.$, a double arsenite-acetate of copper, made by mixing boiling aqueous solutions of arsenious acid and cupric acetate, diluting the mixture with cold water, and setting aside.

Copper compounds, in solid state, recognised by affording red beads or spangles of reduced metal, when heated with carbonate of sodium on charcoal before the blowpipe. Also by rendering the borax bead, heated in the oxidising flame, green when hot, pale blue when cold—heated in the reducing flame, opaque-red or colourless.

Cupric solutions recognised by their blue or green colour. Also, by their giving with sulphuretted hydrogen a black precipitate, insoluble in dilute acids; with ammonia a pale blue preci-

pitate, soluble in excess to form a deep blue solution; and with ferrocyanide of potassium a chocolate-red precipitate. Minute quantities of soluble copper recognised by depositing on a steel needle a coating of red-metal, soluble in ammonia under exposure to air, to form a blue solution precipitable, after acidification with acetic acid, by ferrocyanide of potassium.

(94.) Uranium.

One of the rarer elements. Its only available source the native $\frac{3}{4}$-oxide, or pitchblende U_3O_4. Its occurrence also as uranite $(UO)_4\overset{''}{Ca}P_2O_8.8Aq$, as chalcolite $(UO)_4\overset{''}{Cu}P_2O_8.8Aq$, and as a chief or minor constituent of several other rare minerals.

Uranium obtained in metallic state by heating uranous chloride UCl_2, with sodium. Its production in fused globules, by strongly heating crude product of the reaction in a wind furnace. Uranium a hard, malleable, iron-coloured, very heavy metal, of sp. gr. 18·4; permanent, save for a superficial tarnish, in air; combustible, though with difficulty save when finely divided, at a red heat. Its solubility in dilute hydrochloric and sulphuric acids, with evolution of hydrogen and formation of green uranous solutions. Its attackability by chlorine with combustion; and, at a gentle heat, by sulphur.

Formation by uranium of two series of compounds; a diad or uranous series represented by uranous chloride UCl_2; and a triad or quasi-triad or uranic series represented by uranic oxichloride $\overset{''}{UO}Cl$, the oxide U_2O_3, &c.

URANOUS COMPOUNDS.

Chloride, UCl_2; sole product of the combustion of uranium in chlorine gas; made by strongly heating any uranium oxide, mixed with charcoal, in current of chlorine; or by heating uranous oxide in current of hydrochloric acid. Its occurrence as a sublimate of lustrous dark green octahedrons, volatilisable at a red heat, deliquescent and fuming in moist air. Its dissolution in water,

with heat and hissing noise, to form a dark emerald-green liquid, drying up, in vacuo, into an amorphous, deliquescent, soluble mass. Solution of uranous chloride decomposed by ebullition, or by excess of boiling water, with precipitation of uranous hydrate and liberation of hydrochloric acid.

Hydrate; producible as above, by pouring solution of uranous chloride into excess of boiling water or of dilute alkali. An orange-brown powder, dissolving in acids to form green uranous salts.

Oxide, UO; made by heating the uranic or an intermediate oxide in current of hydrogen; by igniting uranic oxalate *per se*, or preferably in current of hydrogen, &c. A red-brown crystalline powder, of metallic lustre and sp. gr. 10·15. Its combustion when heated in air, to yield the $\frac{3}{4}$-oxide. Crystalline uranous oxide insoluble, the amorphous oxide, procurable by desiccation of the hydrate, soluble in dilute acids.

Uranous solutions recognisable by their dark green colour; by their powerful reducing action as upon gold and silver salts; by their yielding with caustic alkalis a brown precipitate of uranous hydrate, and with sulphide of ammonium, though not with sulphuretted hydrogen, a black precipitate of uranous sulphide.

Existence of an inferior or hypo-uranous chloride, and of a corresponding unstable oxide. The chloride U_2Cl_3 (?), made by igniting uranous chloride in a current of hydrogen or ammonia, as a fibrous dark brown mass, dissolving in water to form an unstable purple solution.

URANIC COMPOUNDS.

Oxichloride, UŐCl; made by passing chlorine over ignited uranous oxide. An orange-yellow vapour, solidifying into a yellow, crystalline, easily fusible mass. Its dissolution in water to form a yellow liquid, also producible by exposure to air of uranous chloride solution. Its combination with alkali metal chlorides to form crystallisable double salts, as UOCl.KCl.Aq, &c. Non-existence of any uranic chloride UCl_3, or other salt corre-

sponding thereto. All uranic salts formed on type of the oxichloride, and derivable from respective acids by substitution of uranous oxide, or uranyl, for basic hydrogen:

HCl	HNO_3	$HKSO_4$	H_2SO_4
$(UO)Cl$	$(UO)NO_3$	$(UO)KSO_4$	$(UO)_2SO_4$

Oxide, U_2O_3; procurable by cautiously heating uranylic nitrate to temperatures below 300°, as a buff yellow powder, dissolving in acids to furnish uranylic salts. Combination of uranic oxide with bases to form definite compounds, known as uranites, mostly referrible to the formula $M_2O.2U_2O_3$ or $\overset{\prime\prime}{M}O.2U_2O_3$. Those of the alkali- and alkaline earth metals, $K_2O.2U_2O_3.3Aq$, and $BaO.2U_2O_3$, producible, by addition of the respective hydrates to uranylic nitrate or chloride solution, as yellow precipitates insoluble in water, insoluble in alkalis, readily soluble in acids, unalterable at a red, but losing some oxygen at a white heat. Presence of small but variable proportion of ammonia (about 2 per cent.) in so-called uranite of ammonia, precipitated by ammonia from dissolved uranylic salts.

Uranous uranite, $UO.U_2O_3$, or uranoso-uranic oxide U_3O_4; found native, as pitchblende, in massive state and more rarely in regular octahedrons, of sp. gr. 6·8, and variable dark greenish colour. Compound obtainable artificially, by gently roasting uranous oxide in air, or by ignition of uranic oxide or nitrate, as a dark green velvety powder. Uranoso-uranic oxide soluble in nitric acid with oxidation into uranylic nitrate. Soluble in tolerably strong hydrochloric and sulphuric acids to form mixed uranous and uranylic solutions, yielding with ammonia a greenish precipitate of uranoso-uranic oxide in hydrated state.

Reduction of the oxide, by strong ignition in air, to leave a black residue, sometimes regarded as a distinct oxide, U_4O_5 or $2UO.U_2O_3$. Its further reduction, by strong ignition with hydrogen, charcoal, or sodium, but only to state of uranous oxide.

Salts. Uranylic nitrate produced in first instance from pitchblende, and employed as a source of all other uranium com-

pounds. Crude pitchblende ignited, quenched, pulverised, re-ignited with a little charcoal, and digested with hydrochloric acid to remove earthy, ferruginous and other impurities. Residue roasted, boiled with nitric acid, and produced nitric acid solution evaporated nearly to dryness, so as to effect further removal of iron in form of ferric arseniate, &c. Soluble salts then extracted with water, the solution, freed from foreign metals by treatment with sulphuretted hydrogen, evaporated to crystallising point, and salt purified by recrystallisation. Uranylic nitrate $(UO)NO_3.3Aq$, thus obtained in fluorescent, bright yellow, prismatic crystals, soluble in water to form a yellow solution, and decomposible by heat to leave uranic oxide and uranoso-uranic oxide successively. The sulphate $(UO)_2SO_4.3Aq$, produced by dissolving the $\frac{1}{4}$-oxide in sulphuric acid, oxidising solution with nitric acid and crystallising. Yellow prisms soluble in water, forming with sulphate of potassium the double salt $(UO)KSO_4.Aq$. The oxalate $(UO)_2C_2O_4.Aq$, thrown down in yellow crystalline grains, on mixing warm saturated solutions of oxalic acid and uranic nitrate, and setting aside. Salt almost insoluble in cold water; decomposed by heat to leave uranous oxide.

Uranylic salts recognisable by their yellow colour. Also, by their solutions giving with caustic alkalis a yellow precipitate; with ferrocyanide of potassium a chocolate precipitate; and with sulphide of ammonium, but not with sulphuretted hydrogen, a brown precipitate. Further reaction of uranylic solutions with the carbonates and especially the acid carbonates of ammonium, potassium, and sodium, to furnish yellow precipitates soluble in excess of the precipitants.

CHAPTER XII.

(95.) Platinum Elements.

Palladium, Rhodium, Ruthenium.

Platinum, Iridium, Osmium.

A well-defined group of metals associated together by their distribution in nature, and by a community of characteristic properties. Symbols and atomic weights:

Pd	Palladium	106·5	Pt	Platinum	197·5
Ro	Rhodium	104	Ir	Iridium	198
Ru	Ruthenium	104	Os	Osmium	199

Specific gravities of palladium, rhodium, and ruthenium, 11·8, 12·0, and 11·4 respectively; of platinum, iridium, and osmium, 21·5, 21·15, and 21·4 respectively.

Metallic osmium hitherto unfused; the other five metals fusible only in the oxihydrogen blowpipe, palladium and platinum the most readily.

Formation by the platinum metals of chlorides corresponding to the typical formulæ, MCl_2, MCl_4, and MCl_3 or M_2Cl_6. Well-marked property of the different chlorides to form double salts with the chlorides of alkali-metal and ammonium, for the most part more stable than double chlorides generally, and some of them very characteristic:

Dichlorides.		Sesqui-chlorides.		Tetrachlorides.	
$PdCl_2$	Palladous	"		$PdCl_4$	Palladic
$PtCl_2$	Platinous	"		$PtCl_4$	Platinic
$RoCl_2$	Hyporhodous (?)	Ro_2Cl_6	Rhodous	$RoCl_4$	Rhodic (?)
$IrCl_2$	Hypiridous (?)	Ir_2Cl_6	Iridous	$IrCl_4$	Iridic
$RuCl_2$	Hyporuthenous	Ru_2Cl_6	Ruthenous	$RuCl_4$	Ruthenic
$OsCl_2$	Hyposmious	Os_2Cl_6	Osmious	$OsCl_4$	Osmic

The dichlorides of palladium and platinum well-defined, that of palladium being indeed its best known compound. The dichlorides of rhodium and iridium rather indicated than actually known. Those of ruthenium and osmium existent, but imperfectly examined.

Non-existence of any sesquichloride of palladium, or of platinum (?). The sesquichlorides of rhodium and iridium their best known and ordinary salts. Those of ruthenium and osmium well-established but unimportant compounds.

Existence of a tetrachloride of rhodium not established. Formation by each of the other metals of a more or less well-defined tetrachloride, that of platinum being its best known and ordinary salt.

The several platinum-metal chlorides readily reducible to the metallic state, most of them, unlike any other metallic chlorides save those of gold, by heat alone. Formation also, by the different platinum metals, of more or less well-defined oxides corresponding to their several chlorides; most of them, like the chlorides, reducible by heat alone, all of them readily reducible.

Additional formation by the metals ruthenium and osmium of the oxides RuO_3 and OsO_3, behaving as anhydrides, and known only when in combination with bases to form salts, as K_2RuO_4, K_2OsO_4, for instance. Doubtful formation of a similar compound by iridium.

Formation also by ruthenium and osmium of the non-salifiable or neutral oxides, RuO_4 and OsO_4 respectively; both of them exceedingly volatile. Non-formation of a tetroxide by any other known element.

A most characteristic property of the metals palladium, platinum, rhodium, and iridium, their difficult oxidisability, save by means of fused alkali, fused nitre, &c. Ruthenium and osmium, however, readily oxidisable by ignition in a current of air; and also far more readily attackable than the other platinum metals by fusion with nitre, to form potassium rutheniate and osmiate respectively.

The sulphides of the platinum metals unimportant compounds,

usually reducible to the metallic state by ignition in a current of air, sometimes by ignition in close vessels.

The platinum metals for the most part very difficultly attackable by liquid reagents; more readily, however, when alloyed with each other or in pulverulent state. Palladium soluble in nitric acid, and platinum in nitro-muriatic acid. Rhodium also, when alloyed with platinum, and iridium when alloyed with platinum or in pulverulent state, slowly dissolved by nitro-muriatic acid.

Native platinum, an alloy of platinum with its associates, the only source of the metal. Its occurrence in grains and small nodules, dispersed through ancient rock detritus, and often associated with native gold, chrome-iron-stone, and ilmenite, &c. Particular varieties of the alloy, poor in platinum, known as native iridium, native iridosmine, &c. Palladium also found, independent of platinum, as a constituent of palladiferous gold dust.

Complete extraction, and separation from one another, of the different metals contained in native platinum, a very difficult, intricate, and variously conducted operation. Outline of most generally approved process given below. Crude platinum, after treatment with nitric and hydrochloric acids separately, to remove foreign metals, exhausted with boiling nitro-muriatic acid. Resulting solution available as a source of platinum, palladium, and rhodium. The undissolved mixed scaly and granular residue, known as iridosmine, available as a source of iridium, rhodium, osmium, and ruthenium; the granular variety being substantially an alloy of iridium with rhodium, and the scaly variety an alloy of iridium with osmium and ruthenium.

Chief portion of platinum precipitated at once from above solution by addition of sal-ammoniac. Remaining platinum and other metals of the filtrate deposited on plate of iron, and redissolved in nitro-muriatic acid. From this second solution a second platinum precipitate thrown down by addition of sal-ammoniac. Finally, metallic platinum obtained by ignition of the sal-ammoniac precipitates.

Solution, left after separation of platinum as above, neutralised with carbonate of sodium. Palladium then precipitated by

addition of mercuric cyanide, and obtained in metallic state by ignition of the washed cyanide precipitate.

Solution, left after separation of the palladium, acidified with hydrochloric acid, mixed with a little common salt, evaporated to dryness, and residue extracted with alcohol of sp. gr. ·837. Rhodio-chloride of sodium alone left, as a red powder yielding metallic rhodium by its ignition in current of hydrogen.

Insoluble iridosmine residues placed in porcelain tube and heated to redness in current of dry air. Osmium converted by the roasting into highly volatile osmic peroxide OsO_4, carried over into series of empty condensing flasks, and finally, to arrest the last traces, through solution of potash. Ultimate production of osmium in metallic state, by igniting the precipitate of reduced osmium and calomel, formed by boiling the osmic peroxide with mercury and hydrochloric acid.

Ruthenium converted by the above roasting into ruthenous oxide, not volatile *per se*, but carried over by the osmic vapours, and deposited in crystalline state upon fragments of porcelain packed on purpose in remote end of the ignition tube. Metal obtained by igniting the oxide in a current of hydrogen.

Residue of iridium and iridium-rhodium, left after the roasting, fused for some time with nitre at a gentle heat, and product treated with water. Iridium and rhodium, in state of pulverulent di- or sesqui-oxides, filtered off, and any osmium not expelled by the roasting left in solution as osmiate of potassium $K_2O.OsO_3$. Above oxides, retaining much potash, boiled for a long time in nitro-muriatic acid, with conversion of the iridium into potassium iridic chloride, a salt almost insoluble in cold water, but readily soluble in boiling water and crystallisable therefrom on cooling. Metal finally obtained by heating the double salt in current of hydrogen.

Insoluble residue of rhodium oxide heated with chloride of sodium in current of chlorine, so as to furnish rhodio-chloride of sodium, purifiable by crystallisation, and reducible by ignition in hydrogen to leave metallic rhodium.

Introduction, by Deville and Debray, of other methods of treating native platinum. An alloy of platinum with iridium and rhodium, well adapted for the construction of chemical utensils, obtained by simply fusing the platinum ore, mixed with a little lime and placed on a shallow lime crucible, by direct action of the oxihydrogen flame. Palladium, ruthenium, and osmium thereby expelled by volatilisation; iron and other foreign metals by oxidation, and reaction with the lime to form a fusible slag.

Or the native platinum fused with galena in a small reverberatory furnace, and oxide of lead added so as to form sulphurous anhydride and metallic lead (*vide* lead-metallurgy). Combination of the platinum with the lead to form a fusible alloy, ladled off from the heavy deposit of unattacked iridosmine. The lead-alloy then cupelled in the ordinary manner, and resulting spongy platinum fused in the oxihydrogen flame.

(96.) Palladium.

Palladium found in native platinum, from mere trace up to 1·5 per cent. or so. Its extraction therefrom already described. Conversion of spongy into compact metal by process of welding, similar to that employed in the case of platinum. (*q. v.*) Occurrence of palladium also in palladiferous gold dust of Brazil and other parts of South America, to extent of from 5 to 10 per cent. of the ore. Such gold dust fused with silver, and resulting alloy granulated. Silver, palladium, copper, and other metals next dissolved away from the gold by nitric acid, and silver precipitated from the nitric acid solution by common salt. Palladium and copper then precipitated together on zinc or iron, redissolved in nitric acid, the solution supersaturated with ammonia, and palladium precipitated from the ammoniacal filtrate by addition of hydrochloric acid, as insoluble hydrochloride of palladamine, furnishing metallic palladium on ignition.

Palladium also found, though very rarely, in distinct grains or crystalline scales associated with native gold or platinum.

Palladium, in massive state, a hard silver-white metal, of con-

siderable elasticity, ductility and tenacity, less infusible than platinum though unaffected by ordinary furnace heats. Its ready fusion by heat of oxihydrogen flame; and eventual volatilisation in greenish vapours. Palladium more oxidisable, and readily attackable by reagents, than platinum. Its formation, when heated to low redness in air, of a superficial oxide, reducible again at higher temperatures. Its solubility in nitric, and easy solubility in nitro-muriatic acid. Its distinctive acquisition of a brown stain, by evaporation from it of a drop of iodine solution. Its ready attackability by fused nitre, caustic alkali, acid sulphate of potassium, &c. Production of a bulky, sooty, indefinite carbide of palladium by heating the metal in a spirit-lamp flame.

Spongy palladium, as obtained by ignition of palladous cyanide or hydrochloride of palladamine, a grey pulverulent mass, rapidly effecting the explosion of mixed oxygen and hydrogen gases. *Vide* spongy platinum.

Free permeability of compact palladium to hydrogen gas, at temperatures far below a red heat. Its impermeability, even at a red heat, to all other gases.

Remarkable absorption of hydrogen by palladium, to extent varying from 500 to 1000 times the volume of the metal, according to its physical condition. Product unaltered in general appearance, &c., and regarded as an alloy of palladium with hydrogenium (Graham).

Hydrogenation of palladium effected by gently heating it in a current of hydrogen; by placing it in contact with zinc dissolving in acid; and by making it act as a negative electrode. Metal dehydrogenised by heating it in air or in vacuo; by immersing it in weakly oxidising liquids; and by making it act as a positive electrode. Absorption of the gas attended by a considerable expansion of the metal; its discharge by an equivalent contraction. Tenacity of hydrogenised product not inferior to that of original metal; its conductivity but slightly diminished, and its paramagnetism decidedly increased.

Existence of numerous palladium alloys, more especially of copper, gold, silver, and tin. The copper alloy containing 4 parts

copper to 1 part palladium, and the gold alloy containing 4 parts gold to 1 part palladium, fairly ductile metals, perfectly white in colour. The silver alloy, containing 2 parts silver to 1 part palladium, a ductile metal not tarnishable on exposure to air. An alloy of 1 part silver with 9 parts palladium used by dentists for construction of artificial teeth supports, &c. Solubility of palladium in melted tin, with formation of a definite compound Pd_3Sn_2, left in brilliant laminæ on dissolving away the excess of tin by hydrochloric acid.

PALLADOUS COMPOUNDS.

Chloride, $PdCl_2$; made by dissolving palladium in hydrochloric acid with a little nitric acid added, and evaporating down. Producible in brown hydrated crystals; and as a black anhydrous mass, fusible in glass vessels, and decomposible at a full red heat into palladium and chlorine. Its combination with potassium chloride to form the double salt $2KCl.PdCl_2$, soluble in cold, freely soluble in hot water, and crystallisable therefrom in yellow-brown four-sided prisms.

Iodide, PdI_2; obtained, by adding iodide of potassium not in excess to palladous chloride solution, as a black precipitate quite insoluble in water, soluble in ammonia and in aqueous iodide of potassium, decomposible by ignition.

Cyanide, $Pd(CN)_2$; made by adding cyanide of potassium or mercuric cyanide to neutral palladous chloride solution, as a yellowish precipitate, soluble in acids, in ammonia, and in aqueous cyanide of potassium. Its production also by boiling mercuric cyanide with oxide of palladium. Its decomposition by heat, to leave metallic palladium in spongy state.

Oxide, PdO; thrown down, in hydrated state, by decomposing palladous chloride with carbonate of potassium, as a dark-brown precipitate, soluble both in acids and alkalis. The anhydrous oxide producible by desiccation of the hydrate; usually obtained by heating the nitrate, as a black residue difficultly soluble in acids, decomposible only upon strong ignition.

Sulphide, PdS; made, in hydrated state, by treating palladous solutions with sulphuretted hydrogen, as a black precipitate insoluble in sulphide of ammonium; and, in anhydrous state, by direct combination of palladium with sulphur. A grey fusible mass, decomposible by long-continued roasting to leave metallic palladium, but not by even strongest ignition in close vessels.

Nitrate, $Pd(NO_3)_2$; made by dissolving spongy palladium in nitric acid and evaporating down. Salt producible as a dark red saline mass, and in prismatic crystals, soluble in small quantity of water, but decomposible by excess of water with precipitation of a basic salt. Its decomposition by ignition to leave palladous oxide.

Sulphate, $PdSO_4$; made by acting on palladous nitrate or oxide with sulphuric acid, as a dark brownish-red, deliquescent, soluble salt.

Ammoniated salts. The di-ammonia chloride $2NH_3.PdCl_2$, producible in two isomeric forms; as a beautiful rose-coloured precipitate, by acting on concentrated palladous chloride solution with slight excess of ammonia; and as an insoluble yellow compound, by heating the moist red precipitate to 100°, or by dissolving it in ammonia and precipitating resultant solution with hydrochloric acid. The yellow compound regarded as hydrochloride of palladamine $N_2H_4Pd.2HCl$ (H. Müller). Its dissolution in potash without evolution of ammonia, even at boiling heat. Its reaction, when digested with silver oxide, to yield the oxide or hydrate $2NH_3.PdO$ or $N_2H_4Pd.H_2O$, as a soluble, strongly alkaline base, precipitating metallic salts, neutralising acids, and absorbing carbonic acid from the atmosphere.

The tetrammonia chloride $4NH_3.PdCl_2$, made by dissolving hydrochloride of palladamine in ammonia. Its separation from the ammoniacal solution in colourless clino-rhombic prisms, decomposible by heat, with evolution of ammonia, to reproduce hydrochloride of palladamine. The corresponding sulphate $4NH_3.PdSO_4$, producible, in small colourless prisms, by treating palladous sulphate with excess of ammonia. The oxide $4NH_3.PdO$ obtained by decomposing the sulphate with hydrate of barium, or

the chloride with oxide of silver, as a soluble, crystallisable, strongly alkaline body, similar in properties to the di-ammonia compound.

PALLADIC COMPOUNDS.

Chloride, $PdCl_4$; formed in solution by dissolving palladous chloride in nitro-muriatic acid or chlorine water. An almost black liquid decomposible, by ebullition or dilution, with separation of chlorine and reproduction of palladous chloride. The double potassium chloride $4KCl.PdCl_4$, thrown down as a reddish crystalline precipitate by addition of potassium chloride to palladic chloride solution. Also by acting on the finely powdered palladous double chloride with nitro-muriatic acid. Its production in minute octahedral crystals. Salt decomposed by ebullition in water, with evolution of chlorine.

Oxide, PdO_2; produced as a yellowish-brown hydrate, retaining some alkali, by decomposing solid potassio-palladic chloride with solution of caustic or carbonated potash. Compound soluble in caustic alkali; rendered anhydrous by ebullition with water, and deposited as a dense black powder difficultly attackable by acids. No corresponding sulphide known.

(97.) Platinum.

Presence of platinum, to extent ranging generally from 75 to 87 per cent., in the crude native metal including its accidental impurities. Usual occurrence of the ore in irregular flattened grains, of all sizes from a small pea downwards. Rare occurrence of larger masses or nuggets. Occasional presence in the ore of fairly pure platinum, crystallised in isolated octahedrons.

Production of spongy platinum, by ignition of the ammonio-chloride, thrown down by addition of sal-ammoniac to solution of native platinum in nitro-muriatic acid, pre-considered. Frequent presence in the crude solution of some iridic chloride, thrown down with the platinic chloride by sal-ammoniac, and recognised by the precipitate being of a pinkish red instead of a pure orange-yellow colour. In event of a portion of the crude

solution, tested with sal-ammoniac, giving a pinkish precipitate, and an iridium-free metal being required, the bulk of the solution precipitated by chloride of potassium instead of by sal-ammoniac, and the resulting potassio-chlorides ignited with carbonate of potassium. Product washed with water, and insoluble residue of metallic platinum and iridous oxide heated with nitro-muriatic acid so as to dissolve the metal and leave the oxide. Two or three repetitions of the process necessary in order to obtain perfectly pure platinum.

Conversion of spongy into malleable platinum sometimes effected now-a-days by its fusion in the oxihydrogen flame, but still most generally by Wollaston's process of welding. The spongy metal rubbed to powder with water in a wooden mortar, the fine platinum mud collected in slightly conical brass moulds, and, the water being strained off, the metal subjected to powerful pressure so as to form it into a coherent cake of sp. gr. about 10. This cake next exposed for some time to strongest heat of a wind furnace; whereby a considerable spontaneous welding together of the particles of metal effected. Resulting mass, of sp. gr. about 17 or 18, then subjected, while still hot, to careful hammering and so obtained of sp. gr. exceeding 21. Process one of considerable delicacy, through liability of the welding to local imperfections.

Platinum in massive state, a lustrous, greyish-white, exceedingly malleable and ductile metal, about equal to copper in hardness and tenacity. Its conduction of heat and electricity very imperfect, inferior to that of iron. Its expansibility by heat far below that of any other malleable metal, and but little higher than that of glass, whence the possibility of fusing glass and it permanently to each other. Platinum according to its physical condition, whether fused or welded, capable of absorbing at a red heat from $\frac{1}{5}$ to 5 times its volume of hydrogen, measured cold. The metal, at a red heat, readily permeable by hydrogen, but quite impermeable by all other gases. Softening of platinum, so as to become weldable, at a strong red heat. Its infusibility in

highest furnace heats; but ready fusion, and even slow volatilisation, in the oxihydrogen flame. Metal not crystallisable artificially, but found native in regular octahedrons.

Platinum inoxidisable by air at any temperature; and unattackable by dry chlorine. Its indifference to nitric acid; and but slow dissolution, unless finely comminuted, in nitro-muriatic acid. Its attackability by fused caustic alkali; and, at a high temperature, by fused nitre and acid sulphate of potassium. Its capability of combining with sulphur, silicon, phosphorus, &c. Frequent injury done to platinum vessels by strongly heating them in contact with mixed charcoal and silica, mixed charcoal and phosphate, &c.

Spongy platinum, as obtained by ignition of ammonio-platinic chloride, a dull grey pulverulent mass, becoming lustrous under the burnisher. Its chemical reactions similar to, but more facile than, those of the compact metal.

Characteristic property of perfectly clean malleable platinum, made dry and warm, and in a more marked degree of spongy platinum, to cause the chemical combination of mixed oxygen and hydrogen gases. Temperature of the metal, and consequently its activity, increased by the constantly accelerated combination, whence its eventual ignition so as to explode the mixture. Similar but less striking results obtained with other gaseous mixtures, as of carbonous oxide and oxygen, marsh gas and oxygen, &c., but not of hydrogen and chlorine.

Platinum producible, by way of precipitation, in state of division and activity surpassing that of the spongy metal. Product, known as platinum black, obtainable by very many reducing processes, as by boiling solution of platinic sulphate with alcohol; boiling solution of platinic chloride with carbonate of sodium and sugar, or with formiate of sodium, &c. Its usual preparation by adding alcohol, little by little, to a boiling solution of platinous chloride in excess of strong potash. Reaction attended by a considerable effervescence of carbonic anhydride, from oxidation of the alcohol, and a precipitation of the correlatively reduced platinum, afterwards washed successively with alcohol, potash, hydrochloric acid and water. Its appearance in dry state as a black

sooty powder, effecting the immediate explosion of mixed oxygen and hydrogen gases; the rapid aërial oxidation of common alcohol vapour and methyl-alcohol vapour into acetic acid and formic acid respectively; and the hydrogenation of prussic acid vapour into methylamine, &c.

Platinum capable of uniting with most of the metals to form more or less fusible alloys. Combinations of the spongy metal with lead, antimony, bismuth, &c., attended with considerable development of heat, and occasionally with incandescence. Platinum not wetted by mercury, but readily by sodium amalgam. Alloy of 1 part platinum and 2 parts silver used for dentists' fittings; and, in form of wire, as a measure of electric resistance. Unlike gold, platinum when alloyed with excess of silver, completely soluble in nitric acid. Alloy of 7 parts platinum and 3 parts gold infusible by strongest heat of a wind furnace, and sometimes used for construction of small crucibles, &c. Dissolution of platinum in melted tin to form a definite compound Pt_2Sn_3, left, after slow cooling of the mass and its ebullition with hydrochloric acid to remove excess of tin, in geode-like masses lined with cubes or nearly cubical rhombohedrons.

PLATINOUS COMPOUNDS.

Chloride, $PtCl_2$; made by heating dry platinic chloride to about the melting point of tin, 230°, so long as chlorine continues to be evolved. A dark greenish powder; decomposed into its constituents by ignition; insoluble in, and unwetted by water; unacted on by sulphuric and nitric acids; soluble in boiling hydrochloric acid, probably as the compound $2HCl.PtCl_2$; soluble in platinic chloride solution to form an almost black liquid, probably containing the sesquichloride Pt_2Cl_6. The double salt $2KCl.PtCl_2$, obtained by adding potassium chloride to above hydrochloric acid solution and evaporating. Its deposition in red anhydrous four-sided prisms, isomorphous with those of corresponding palladium compound.

Oxide, PtO. Solid platinous chloride soluble in excess of potash to form a dark olive green liquid, yielding on neutralisa-

tion with sulphuric acid a black precipitate of hydrated platinous oxide, dissolving in acids to form unstable salts. Its ready decomposition by heat to leave metallic platinum.

Sulphite, $PtSO_3$; produced as a dark greenish solution, by passing sulphurous anhydride through hydrated platinous oxide suspended in water; also, together with hydrochloric and sulphuric acids, by passing sulphurous anhydride through boiling solution of platinic chloride. Its combination with alkali sulphites to form colourless, crystallisable, double salts, as $(NH_4)_2Pt(SO_3)_2.Aq$, best prepared by neutralising either of the above solutions with ammonia.

PLATINIC COMPOUNDS.

Chloride, $PtCl_4$; made by dissolving platinum in nitromuriatic acid and evaporating solution to dryness at 100°. A deliquescent brown mass, soluble in water to form an orange solution, and also in alcohol and ether. Decomposition of the salt at 230°, to leave platinous chloride; and by ignition, to leave metallic platinum. Solution reducible at boiling heat by sulphurous anhydride to leave platinous sulphite &c., and by alkali formiate to furnish platinum-black.

Combinations of platinic chloride with alkali chloride &c. Presence in ordinary platinic chloride solution, of the hydrogen compound $2HCl.PtCl_4$ (?). The ammonium salt $2NH_4Cl.PtCl_4$, formed, by mixing sal-ammoniac and platinic chloride solutions, as an orange-yellow crystalline precipitate, sparingly soluble in cold water, soluble in boiling water and crystallisable therefrom in orange octahedrons, insoluble in alcohol and ether. Its ready decomposition by ignition, to leave metallic platinum in spongy state. The potassium salt $2KCl.PtCl_4$, a similar and isomorphous compound, somewhat less soluble in water, and requiring a very strong heat for its complete decomposition. The rubidium and cæsium double salts, insoluble even in boiling water. The sodium salt $2NaCl.PtCl_4.6Aq$, soluble in water, alcohol, and ether, and crystallisable in fine orange-yellow needles.

Oxide, PtO. Action of sulphuretted hydrogen, on platinic chloride or sodio-platinic chloride solution, to throw down a brown-black precipitate of platinic sulphide PtS_2, soluble in alkali sulphides, decomposible by ignition to leave metallic platinum, oxidisable by nitric acid (and partially by gentle heating in air) to form platinic sulphate. Double decomposition of platinic sulphate and barium nitrate, to form platinic nitrate solution. Hydrated platinic oxide $2H_2O.PtO_2$, thrown down from the nitrate solution, by carbonate of sodium in deficit, as a bulky ochre-like precipitate. With addition of more than half the quantity of carbonate of sodium required for complete precipitation of the nitrate, an indefinite basic compound formed. Solubility of platinum hydrate in excess of alkali, to form a crystallisable platinite, as $Na_2O.3PtO_2.6Aq$. The oxide procurable from the hydrate at a gentle heat, and reducible to the metallic state on ignition. Its dissolution in mineral acids to form platinic salts.

PLATIN-AMMONIA COMPOUNDS.

Formation by platinum of four principal series of ammonia compounds, referrible respectively to the four chlorides, formulated, quoad their ultimate composition, as follows:

	Di-ammonia Salts.	Tetrammonia Salts.
Platinous	$2NH_3.PtCl_2$	$4NH_3.PtCl_2$
Platinic	$2NH_3.PtCl_4$	$4NH_3.PtCl_4$

Ammonia platinic compounds not producible directly from platinic chloride &c.; but by oxidation or chlorination of corresponding di- and tetra- ammonia platinous compounds.

Tetrammonia compounds, platinous and platinic, producible from corresponding di-ammonia compounds by action of ammonia; and di-ammonia compounds reproducible from corresponding tetrammonia compounds by expulsion of ammonia.

Diammonia platinous chlorides &c. The salt $2NH_3.PtCl_2$, produced, on adding excess of ammonia to hydrochloric acid solution of platinous chloride, as a bright dark green precipitate,

composed of acicular crystals, insoluble in water and in hydrochloric acid (green salt of Magnus).

Dissolution of green salt of Magnus by its ebullition with aqueous nitrate or sulphate of ammonium; and separation on cooling of a crystallised yellow salt, isomeric with original salt of Magnus.

Both salts producible in many other ways. Under certain conditions, a garnet-red crystalline compound also obtained, as a third distinct isomer (?).

The different isomers conceivable as being derived from two units of hydrochloride of ammonia; by a substitution of one atom of diad platinum for two atoms of hydrogen in the hydrochloric acid, or for two atoms of hydrogen in the ammonia, or for one atom of hydrogen in the ammonia and one atom in the hydrochloric acid:

$$\begin{matrix} NH_3 \\ NH_3 \end{matrix} . \overset{\prime\prime}{Pt}Cl_2 \qquad \begin{matrix} NH_3 \\ NH_2 \end{matrix} \overset{\prime\prime}{Pt} \begin{matrix} Cl \\ HCl \end{matrix} \qquad \begin{matrix} NH_2 \\ NH_2 \end{matrix} \overset{\prime\prime}{Pt}.H_2Cl_2$$

Existence of an oxide (Reiset's second base), a nitrate, a sulphate, &c., having the empiric formulæ $2NH_3.PtO$, $2NH_3.Pt(NO_3)_2$ and $2NH_3.PtSO_4$ respectively, all corresponding to the yellow chloride or hydrochloride, $2NH_3.PtCl_2$ or $N_2H_4Pt.2HCl$; *vide infra.*

Tetrammonia platinous chlorides &c. The salt $4NH_3.PtCl_2$, obtained, in bulky yellowish monohydrated crystals, by boiling up green salt of Magnus in ammonia until dissolved, and setting liquid aside. Non-liberation of ammonia from the salt by its treatment with potash in the cold, scarcely even upon ebullition. Its reaction with platinous chloride to reproduce green salt of Magnus. Its desiccation at a little over 100°; and evolution of ammonia at higher temperatures to leave the isomeric yellow salt $2NH_3.PtCl_2$. Its reactions with nitrate and sulphate of silver respectively, to produce the nitrate $4NH_3.Pt(NO_3)_2$, and sulphate $4NH_3.PtSO_4$, as crystallisable salts. Decomposition of the sulphate by exact sufficiency of baryta water to form the hydrate $4NH_3.Pt(HO)_2$ (Reiset's first base), obtainable in deliquescent soluble needles, alkaline, caustic, and rapidly absorptive of carbonic acid.

Action of heat on Reiset's first base to expel water and ammonia, leaving his second base $2NH_3.PtO$, as a greyish mass, reacting with hydrochloric, nitric, and sulphuric acids, &c., to form the yellow salts; *vide supra.*

Diammonia platinic chlorides, &c. The salt $2NH_3.PtCl_4$, producible, as a soluble crystalline compound, by continued action of chlorine on green salt of Magnus $2NH_3.PtCl_2$, suspended in water. An isomeric modification, insoluble in cold and but sparingly soluble in hot water, similarly producible by acting on the yellow salt $2NH_3.PtCl_2$, with chlorine.

Successive production from latter insoluble compound of an oxynitrate $2NH_3.PtO(NO_3)_2$, by boiling it with nitrate of silver; of a nitrate $2NH_3.Pt(NO_3)_4$, by crystallising the oxynitrate from nitric acid; and of the oxide $2NH_3.PtO_2$ (Gerhardt's base), by precipitating the nitrate with ammonia, as a yellowish crystalline powder, made up of small rhomboidal prisms, insoluble in water, but dissolving in acids to form di-ammonia platinic salts.

Tetrammonia platinic chlorides, &c. The salt $4NH_3.PtCl_4$, produced by action of chlorine on the platinous salt, $4NH_3.PtCl_2$; by action of ammonia on above insoluble platinic salt $2NH_3.PtCl_4$; and by action of hydrochloric acid on salt of Gros $4NH_3.PtCl_2(NO_3)_2$; *vide infra.*

Its occurrence in transparent white, regular octahedrons, sparingly soluble in hot water; decomposible by heat, with evolution of ammonia and reconversion into the insoluble di-ammonia platinic chloride.

The nitrate-chloride $4NH_3.PtCl_2(NO_3)_2$ (salt of Gros), obtained, with reduction of platinum, by acting on green salt of Magnus with nitric acid:

$$2(2NH_3.PtCl_2) + 2HNO_3 = 4NH_3.PtCl_2(NO_3)_2 + Pt + 2HCl$$

Salt deposited as an almost white powder, soluble in boiling water, and crystallising on cooling in shining, flattened, pale-yellow prisms. Its susceptibility of double decomposition, with exchange of nitric for other acid radicals to form the oxalate-chloride, sulphate-chloride, and above chloride-chloride, &c.

Only half the chlorine of the chloride, and none whatever of the nitrate-chloride, precipitable by nitrate of silver. Constitution of platinic, in relation to platinous, ammonia-salts probably in accordance with following expressions:

$$N_2H_4\overset{''}{Pt}.2HCl \qquad N_4H_{10}\overset{''}{Pt}.2HCl$$

$$\left.\begin{matrix}N_2H_4\overset{iv}{Pt}\\Cl_2\end{matrix}\right\}2HCl \qquad \left.\begin{matrix}N_4H_{10}\overset{iv}{Pt}\\Cl_2\end{matrix}\right\}2HCl \qquad \left.\begin{matrix}N_4H_{10}\overset{iv}{Pt}\\Cl_2\end{matrix}\right\}2HNO_3$$

A double nitrate-oxichloride, $8NH_3.Pt_2\ddot{O}Cl_2(NO_3)_4$ or $\left.\begin{matrix}N_8H_{20}\overset{vi}{Pt_2}\\Cl_2O\end{matrix}\right\}4HNO_3$ (salt of Raewsky), produced instead of the simple nitrate-chloride, by boiling green salt of Magnus with large excess of nitric acid. Its deposition on evaporation of the liquid, in small brilliant needles.

(98.) Rhodium.

Presence of rhodium, from a mere trace up to 2·5 per cent. or so, in native platinum; dissolving, with the platinum, in nitro-muriatic acid. Existence of additional rhodium in insoluble residue of iridosmine. Its proportion in this residue very variable; dependent upon relative amount of scaly and granular compound in the sample, the latter alone being rich in rhodium.

Rhodium a white, very hard, usually brittle, but in its pure state malleable metal; less readily weldable and more infusible than platinum; soluble, when alloyed with certain other metals, but in its isolated state, quite insoluble, even in nitro-muriatic acid. Rhodium far more oxidisable than platinum. Considerable oxidation, especially of the unfused pulverulent metal, heated to bright redness in current of air. Its ready attackability by fused caustic alkali, mixed nitre and pearlash, and acid sulphate of potassium. Its conversion, by ignition with common salt in current of chlorine, into sodium rhodous chloride.

Hyporhodous compounds but little known. Existence of the chloride $RoCl_2$, doubtful. The oxide RoO, producible by igniting hydrated rhodous oxide; and the sulphide RoS, by combustion of rhodium in sulphur vapour.

Rhodous compounds. The double sodium rhodous chloride $6NaCl.Ro_2Cl_6$, formed by action of chlorine on ignited rhodium (or any rhodium oxide) and common salt; also by evaporation of mixed rhodous chloride and common salt solutions. Its insolubility in alcohol; and crystallisability from hot water in cherry-red, anorthic, hydrated prisms. Existence of similar potassium and ammonium double chlorides, $6KCl.Ro_2Cl_6.6Aq$; $4KCl.Ro_2Cl_6.2Aq$; and $6NH_4Cl.Ro_2Cl_6.3Aq$. Rhodous chloride formed in hydrated state, by precipitating solution of the double potassium-salt with hydro-fluosilicic acid, and evaporating the filtrate. A nearly black, amorphous, deliquescent mass, dissolving in water to form rose-red solution, and decomposing by strong ignition into chlorine and rhodium. Most rhodous salts of a rose-red colour, but some of them inexplicably yellow.

Production, on adding potash to dissolved sodium rhodous chloride, of a yellow precipitate, retentive of much potash and dissolving in excess of the precipitant. From resulting solution, boiled with strong potash or treated with alcohol, hydrated rhodous oxide $Ro_2O_3.3H_2O$, thrown down as a brown precipitate, at first gelatinous, but soon becoming compact, and difficultly soluble in hydrochloric acid. The anhydrous oxide Ro_2O_3, made by dissolving above yellow precipitate in nitric acid, evaporating to dryness, washing out nitrate of sodium with alcohol, and igniting the residue. A grey porous mass, insoluble in acids, reducible at a gentle heat by hydrogen.

A rhodammonic chloride $10NH_3.Ro_2Cl_6$, analogous in composition to purpuro-cobaltic chloride $10NH_3.Co_2Cl_6$, made by supersaturating rhodous chloride, or ammonium rhodous chloride, with ammonia, and evaporating. Yellow crystalline powder deposited, almost insoluble in water, slowly and imperfectly alterable by acids, crystallisable from aqueous ammonia, and decomposible by ignition to leave metallic rhodium.

Rhodic compounds. The chloride $RoCl_4$, unknown; the oxide RO_2, produced in anhydrous state by heating rhodium or rhodous oxide with nitre, and digesting product in nitric acid to remove potash. The hydrated oxide $RoO_2.2H_2O$, made by action of

chlorine on potash solution of yellow rhodous hydrate. A green powder, soluble in hydrochloric acid with evolution of chlorine and formation of red rhodous chloride. Filtrate from green hydrate of a fine violet blue colour, gradually becoming colourless and depositing a blue precipitate, possibly the teroxide RoO_3.

(99.) Iridium.

Presence in most native platinum of about 1 per cent. of iridium, soluble with the platinum in nitro-muriatic acid, and also precipitable therewith by sal-ammoniac. Chief source of iridium, however, the residue of iridosmine left undissolved by nitro-muriatic acid. Amount of this residue very variable, usually about 2 per cent., occasionally 6 or 7 per cent., and, in particular specimens, 25 to 35 per cent. Iridosmine also found in distinct grains or laminæ, apparently hexagonal, associated with native platinum, and sometimes constituting the chief portion of the platinum ore. Usual proportion of iridium in iridosmine from 50 to 70 per cent. Iridium also found, nearly free from osmium, but alloyed with platinum or platinum and rhodium, in cubo-octahedral crystals as native iridium.

Iridium, a white, brittle, extremely hard metal, less readily and completely weldable, and far less readily fusible than platinum. Unfused metal slowly dissolved by nitro-muriatic acid, and oxidised by ignition in air; but the fused metal insoluble and inoxidisable. Iridium, however, like rhodium, readily attackable by fusion with caustic alkali, with mixed nitre and pearlash, and with acid sulphate of potassium. Also by ignition with chloride of sodium in current of chlorine.

Hypiridous compounds but little known. Production of a complex crystalline red salt $K_8\breve{I}r_2\left\{\begin{matrix}Cl_6\\(SO_3)_3\end{matrix}\right..12Aq$, by reducing potassium iridous chloride with potassium acid sulphite and evaporating. Decomposition of the salt by caustic or carbonated alkali, out of access of air, to yield the oxide IrO, as a black rapidly oxidising precipitate. Hypiridous sulphide IrS, per-

manent at a red heat in close vessels, and left by ignition of the higher sulphides. Hypiridous chloride $IrCl_2$, produced, by cautious heating of the higher chlorides, as an indefinite brown residue, soluble in carbonate of ammonia. Formation, on just acidifying resultant solution with hydrochloric acid, of the diammonia compound $2NH_3.IrCl_2$, as a yellow granular deposit; convertible, by ebullition with ammonia, into the white crystalline tetra-ammonia compound $4NH_3.IrCl_2$.

Iridous compounds. The oxide Ir_2O_3, producible from the double potassium iridous or iridic chloride, by its ignition with carbonate of sodium in current of carbanhydride. A bluish-black powder, insoluble in acids, reducible *per se* only under strong ignition, easily reducible by hydrogen. Iridous chloride obtained in first instance from the compound formed by heating iridium with nitre. Fused mass treated with water, potash just saturated with nitric acid, resulting precipitate dissolved in boiling hydrochloric acid, and solution evaporated down. Product of iridous chloride Ir_2Cl_6, a black deliquescent mass, dissolving in water to form a green solution, and combining with alkali-metal chlorides to form the soluble, crystallisable, dark green, double salts $6NaCl.Ir_2Cl_6.24Aq$, $6KCl.Ir_2Cl_6.6Aq$, $4KCl.Ir_2Cl_6.2Aq$, and $6NH_4Cl.Ir_2Cl_6.6Aq$. These double iridous chlorides also obtainable by reducing the double iridic chlorides with sulphurous acid. An iridos-ammonic chloride $10NH_3.Ir_2Cl_6$, corresponding to the rhodammonic compound, produced, as a flesh-coloured crystalline powder, by prolonged digestion of above ammonium iridous chloride in aqueous ammonia.

Iridic compounds. The chloride $IrCl_4$, corresponding to platinic chloride $PtCl_4$, made by dissolving pulverulent iridium, or potash-free product of its fusion with nitre, in nitro-hydrochloric acid and evaporating. A dark red, almost black, amorphous deliquescent mass, dissolving in water to form a reddish yellow solution. The double iridic chlorides of ammonium, potassium, and sodium made by addition of the several alkali chlorides to iridic chloride solution. The two latter compounds also producible by action of chlorine on ignited mixture of iridium or

iridium oxide with sodium or potassium chloride. The potassium salt $2KCl.IrCl_4$, like the corresponding platinic compound, almost insoluble in cold water, soluble in boiling water, and crystallisable therefrom in anhydrous octahedrons, having an almost black colour, and yielding a reddish powder. The ammonium salt similarly characterised, but crystallisable with an atom of water $2NH_4Cl.IrCl_4.Aq$. Precipitated ammonium platinic chloride occasionally buff- or even pink-tinted from contamination with this salt. The sodium chloride $2NaCl.IrCl_4.6Aq$, freely soluble in water, and crystallisable in black tables and prisms. All three salts reducible to state of green soluble iridous chlorides by action of sulphurous acid. Iridic oxide IrO_2, obtainable by gently heating the hydrate, as a black powder difficultly soluble in hydrochloric acid. The hydrate $IrO_2.2H_2O$, thrown down, as an indigo-blue precipitate, on boiling iridic chloride, or potassium or sodium iridic chloride, with caustic potash. Same precipitate producible with corresponding iridous chlorides, as a result of oxidation. Dissolution of the hydrate in acids to form, save in the case of hydrochloric acid, indefinite salts. The sulphate reducible by ebullition with alcohol, to yield iridium in state corresponding to that of platinum black.

A teroxide of iridium IrO_3, producible in combination with potash, by prolonged ignition of iridium and nitre, as a black crystalline powder, soluble in hydrochloric acid with evolution of chlorine.

Existence of iridic tetrammonia compounds, $4NH_3.IrCl_4$ and $4NH_3.IrCl_2(NO_3)_2$, corresponding to the platinum salts of Gros, the former violet, the latter yellow, and both of them crystallisable from hot water. Chlorine of the violet chloride only half precipitable, and that of the yellow chloride-nitrate not precipitable by nitrate of silver. Latter salt made from the hypiridous compound $4NH_3.IrCl_2$ by boiling it with nitric acid, and former salt from the latter by boiling it with hydrochloric acid.

(100.) Ruthenium.

The least abundant, and last discovered of the platinum metals, found associated with osmium in scaly variety of iridosmine, to

extent of 6 or 7 per cent. A hard, white, brittle, very refractory metal, fusible with extreme difficulty in oxihydrogen flame. Its insolubility in nitro-muriatic acid, and non-attackability by fused acid sulphate of potassium. Its oxidation, however, when heated in current of air to yield ruthenous oxide, irreducible to metallic state *per se*, even at a white heat. Its ready oxidation also, when fused with caustic alkali or with nitre and carbonated alkali, to yield soluble potassium rutheniate. Its combination with tin to form the alloy $RuSn_2$ (?), crystallising readily in perfectly regular cubes.

Hyporuthenous compounds. The chloride $RuCl_2$, formed by igniting the pulverulent metal in chlorine, as a non-volatile, black, crystalline residue, insoluble in acids. The chloride obtained in solution, as a deep blue liquid, by reducing dissolved ruthenous chloride. The oxide RuO, obtained by igniting the chloride with carbonate of sodium in atmosphere of carbanhydride. A metallic-looking, dark-grey powder, unaffected by acids, oxidisable when heated in air, and reducible at ordinary temperatures by hydrogen.

Ruthenous compounds. The chloride Ru_2Cl_6, produced (together with preceding non-volatile chloride) as a brown crystalline sublimate, by heating the pulverulent metal in chlorine. Obtained in solution by dissolving precipitated ruthenous oxide in hydrochloric acid and evaporating. A yellow-brown, semi-crystalline, deliquescent mass, dissolving in water to form an orange-yellow solution. Its combination with chlorides of potassium and ammonium to form the double salts $4KCl.Ru_2Cl_6$, and $4NH_4Cl.Ru_2Cl_6$ respectively. Ruthenous oxide Ru_2O_3, formed by heating the pulverulent metal in air, as a bluish-black powder, insoluble in acids, unaffected by ignition, reducible at a gentle heat by hydrogen. The hydrated oxide thrown down as a black precipitate, by acidifying potassium rutheniate solution with nitric acid; also by precipitating ruthenous chloride solution with carbonate of potassium.

Ruthenic compounds. The isolated chloride $RuCl_4$, unknown. The double potassium and ammonium chlorides,

$2KCl.RuCl_4$ and $2NH_4Cl.RuCl_4$ respectively, produced by dissolving the corresponding ruthenous compounds in nitro-muriatic acid and evaporating. Brownish-rose salts, insoluble in alcohol, very soluble in water, forming brown-rose solutions. The hydrated oxide $RuO.2H_2O$, thrown down by sodium carbonate from above potassium ruthenic chloride, as a gelatinous brown precipitate dissolving in acids to form brown-rose solutions. The anhydrous oxide RuO_2, obtained as a black powder by roasting the corresponding sulphide RuS_2, thrown down from ruthenic solutions by sulphuretted hydrogen.

Rutheniate compound. The potassium salt $K_2O.RuO_3$, formed with great facility by fusing pulverulent ruthenium with nitre or mixed nitre and pearlash. A yellow mass, dissolving completely in water to form an orange-yellow solution, yielding with nitric acid a black precipitate of hydrated ruthenous oxide $Ru_2O_3.xAq$.

Per-ruthenic oxide, RuO_4; produced from potassium rutheniate, by passing a current of chlorine through its concentrated solution. Oxide volatilised, at first by heat of reaction, afterwards by gently warming, and condensed as an irregular yellow sublimate, fusible under water to form on cooling a golden-yellow crystalline mass, heavier than oil of vitriol, volatilising with marked nitrous odour at ordinary temperatures, melting at 58° into a yellow liquid, and boiling at 100°. Per-ruthenic oxide but sparingly soluble in water; soluble apparently without change in hydrochloric acid, to form a solution readily reducible by alcohol, sulphurous acid, &c. Its reaction with strong potash, to yield potassium rutheniate and oxygen, attended with considerable development of heat effecting volatilisation of unaltered peroxide. Its solution in cold dilute potash changed into one of potassium rutheniate on ebullition.

(101.) Osmium.

Its existence in scaly iridosmine, to amount varying from 20 to 50 per cent. Its production, in pulverulent state, as already

described; and in friable lumps, by strong ignition of the precipitated sulphide (Deville and Debray). Metal infusible at any temperature hitherto attained; but rendered compact by intense ignition in oxihydrogen flame, with partial volatilisation. Occurrence of compact osmium in greyish masses, becoming lustrous under the burnisher. Osmium especially characterised by its oxidisability in air, at temperatures varying with its compactness, to yield vaporised perosmic oxide. The pulverulent metal capable of being set fire to, and of burning continuously till entirely consumed. The most compact metal scarcely oxidisable at fusing point of zinc, but combustible at higher temperatures. Osmium combustible also in sulphur vapour. Compact osmium unaffected by boiling nitro-muriatic acid; but the pulverulent metal slowly attacked, with production of vaporous perosmic oxide. Solubility of osmium in strongly heated tin, and its separation therefrom, on slow cooling, as a hard crystalline powder, left by dissolution of the tin in hydrochloric acid.

Hyposmious compounds. Formation, by igniting osmium in dry chlorine, of hyposmious chloride $OsCl_2$, as a blue-black (and of osmic chloride $OsCl_4$, as a more volatile red), deliquescent, crystalline sublimate. Its solubility in water to form a violet solution, producible also by reduction of the superior chlorides and oxidisable into them by mere exposure. Its combination with potassium chloride to form a double salt, of somewhat greater stability. Hyposmious sulphite $OsO.SO_2$, obtained by reducing osmic chloride solution with sulphurous acid, and either evaporating down or boiling with sulphate of sodium. Deposit spontaneously oxidisable when moist, permanent when dry, insoluble in water, soluble in hydrochloric acid without evolution of sulphurous acid to form a violet-blue liquid. Hyposmious oxide OsO, obtained anhydrous by heating above sulphite in current of carbanhydride. The hydrate $OsO.H_2O$, thrown down on boiling the acidulous sulphite solution with excess of potash out of access of air, as a blue-black precipitate oxidising rapidly on exposure, and dissolving in acids to form violet-blue solutions.

Osmious compounds. The chloride Os_2Cl_6, not isolable,

formed as a red-brown solution by dissolving the hydrated oxide in hydrochloric acid. Also by admixture of the other two chlorides, $OsCl_2$ and $OsCl_4$; and by oxidation of the one or reduction of the other. Potassium osmious chloride $6KCl.Os_2Cl_6.6Aq$, a soluble salt, crystallisable in dark red-brown prisms; produced (together with potassium osmic chloride) by heating mixture of pulverulent osmium and potassium chloride in chlorine gas. Formation from double salt of the black anhydrous oxide Os_2O_3, by its ignition with sodium carbonate in atmosphere of carbanhydride; and of the hydrated oxide as a yellow-brown precipitate, by decomposing solution of the salt with caustic alkali.

Osmic compounds. The chloride $OsCl_4$, sublimed, as a dark red floury powder, by igniting osmium in chlorine gas. Its absorption of moisture from the air, and solubility in water to form a yellow solution, decomposible on ebullition or excessive dilution, with formation of perosmic oxide retained in solution and an inferior oxide precipitated. Its combination with alkali-chlorides to form double salts; that of potassium, also produced by igniting the pulverulent metal with chloride of potassium and excess of chlorine, sparingly soluble in water, and crystallisable in anhydrous brown octahedrons $2KCl.OsCl_4$, yielding a scarlet powder. The sodium double chloride $2NaCl.OsCl_4$, obtained by heating osmium sulphide with common salt in a current of chlorine. Its free solubility in water, and crystallisability in orange-coloured prisms, an inch or so long (Claus). The ammonium salt $2NH_4Cl.OsCl_4$, prepared from the sodium salt by precipitation with sal-ammoniac, and deposited in minute octahedrons. The hydrated oxide $OsO_2.2H_2O$, obtained, as a black precipitate, by decomposing solution of the sodium or other double chloride with caustic potash at a boiling heat; or preferably by mixing solution of potassium osmiate with nitric acid. The anhydrous oxide obtained by heating above hydrate, or a mixture of alkali-metal double chloride with sodium carbonate, in an atmosphere of carbanhydride. As obtained from the hydrate, a shining coppery-red mass; as obtained from the double chloride, a dull black powder; both products alike insoluble in acids.

Osmiate compounds. The oxide OsO_3, not isolable. Potassium osmiate $K_2OsO_4.Aq$ or $K_2O.OsO_3.Aq$, producible by fusing osmium with caustic alkali or nitre, and crystallisable from solution of the product; also by dissolving hydrated osmic oxide OsO_2, in potash solution of the peroxide OsO_4. Best made by reducing potash solution of the peroxide with alcohol or potassium nitrite. Its precipitation at once by means of alcohol, as a rose-red crystalline powder; and its gradual deposition by means of the nitrite, in well-defined octahedrons. Its solubility in water to form a rose-coloured solution. Sodium osmiate, a similar but more soluble and non-crystallisable salt. Solutions of both salts decomposible by all acids, with precipitation of osmic oxide and retention of the peroxide in solution:

$$4HNO_3 + 2(K_2O.OsO_3) = 4KNO_3 + 2H_2O + OsO_2 + OsO_4$$

No osmiate of ammonium known. Decomposition of alkali osmiate solutions by sal-ammoniac, with formation of an insoluble, yellow, double salt of ammonic chloride and osmiate oxi-diamide $NH_4Cl.Os\left\{\begin{matrix}O_2\\(NH_2)_2\end{matrix}\right.$, decomposible by ignition in hydrogen to leave metallic osmium.

Perosmic compounds. The oxide OsO_4, formed in dry way, as a crystalline sublimate, by heating osmium or its lower oxides in current of air; and, in moist way, by acting on pulverulent osmium, potassium osmiate, or the intermediate oxides, with nitric or nitro-muriatic acid, and distilling. About one-third of the original distillate redistilled, supersaturated with potash and briskly boiled, so as to drive off the dissolved perosmic oxide, condensable partly in large beautiful crystals, partly in state of concentrated solution. Osmic peroxide usually obtained as a sublimate of colourless, transparent, acicular crystals, softening by the heat of the hand; and melting considerably below 100° into a colourless liquid, boiling at a little above the melting point. The solid peroxide possessed of a characteristic chloride of sulphur-like smell. The vapour intolerably pungent, irritative of the eyes and nose, and highly poisonous. Slow but con-

siderable dissolution of perosmic oxide in water, to form a colourless strong-smelling liquid, devoid of acid reaction, capable of acting as a powerful oxygenant upon ammonia, alcohol, indigo, iodide of potassium, &c.:

$$4NH_3 + 3OsO_4 = N_4 + 6H_2O + 3OsO_2$$
$$\text{and} \quad 10NH_3 + 3OsO_4 = N_4 + 16H_2O + 3(OsO_2.2NH_3)$$

Reaction, however, of sulphuretted hydrogen with the aqueous solution, to furnish an immediate black precipitate of hydrated perosmic sulphide OsS_4. Solubility of perosmic oxide in fixed caustic alkalis, without neutralising them, to form solutions having a yellow colour (from partial deoxidation?), and giving off the greater part of their peroxide upon ebullition, the remainder being resolved into potassium osmiate and free oxygen.

Reaction of warm potash solution of perosmic oxide with ammonia, to yield a yellow crystalline precipitate of potassium osmiamate $KNOsO_3$:

$$H_3N + KHO + OsO_4 = 2H_2O + Os\left\{\begin{matrix}O_3\\NK\end{matrix}\right. \quad \text{or} \quad Os\left\{\begin{matrix}O_3K\\N\end{matrix}\right.$$

Silver salt obtainable from the potassium salt by precipitation with nitrate of silver, and aqueous acid obtainable from the silver salt by its decomposition with hydrochloric acid. Osmiamic acid, $HNOsO_3$ or $Os\left\{\begin{matrix}O_3\\NH\end{matrix}\right.$, thus produced as an unstable, strongly acid solution, decomposing carbonates and even chlorides with effervescence. The potassium salt $KNOsO_3$, soluble in water, crystallisable in square octahedrons, unalterable at 180°, explosive at higher temperatures, and decomposible, by ebullition with hydrochloric acid and chloride of potassium, to yield chlorine and the double osmious chloride $6KCl.Os_2Cl_6$. The silver salt $AgNOsO_3$, thrown down as a lemon-yellow crystalline precipitate, slightly soluble in water and dilute nitric acid, blackening under exposure to light, and exploding at a gentle heat or upon ignition. Existence of several other well-defined osmiamates.

SPOTTISWOODE AND CO., PRINTERS, LONDON AND WESTMINSTER